Aspects of accurate, relativistic quantum chemical calculations

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The Dirac-Fock-Breit Hamiltonian is an excellent, but not complete, description of electronic systems. The largest missing piece is QED, that also can be independently estimated. An interesting test case are the M-C distances in the monocyanides MCN, M=Cu-Au [1]. These calculations were very recently improved [2] and the M=Au case may show preliminary evidence for QED effects.

Another case that we have pushed to the MP2 basis-set limit are the metallophilic test systems $[P(AuPH_3)_4]^+$ [3].

A task requiring as accurate calculations as possible are the determinations of nuclear quadrupole moments, eQ, from experimental quadrupole coupling constants, e^2Qq/h, and calculations of the electric field gradient, eq. The latest review is [4].

The author's latest reviews on the physical fundamentals and chemical applications of relativistic calculations are [5] and [6], respectively.

[1] P. Zaleski-Ejgierd, M. Patzschke, P. Pyykkö, J. Chem. Phys. **128** (2008) 224303.

[2] J. G. Hill, A. O. Mitrushchenkov, K. A. Peterson, J. Chem. Phys. **138** (2013) 134314.

[3] P. Pyykkö, P. Zaleski-Ejgierd, J. Chem. Phys. **128** (2008) 124309.

[4] P. Pyykkö, Mol. Phys. **106** (2008) 1965.

[5] P. Pyykkö Chem. Rev. **112** (2012) 371.

[6] P. Pyykkö, Ann. Rev. Phys. Chem. **63** (2012) 45.