



Scientific Computing & Modelling

Spectroscopy: Magnetic Circular Dichroism, resonance Raman, Mössbauer, Nuclear Resonance Vibrational Spectroscopy, Electric Field Gradient for solids

Analysis: Atoms In Molecules (AIM) and Electron Localization Function (ELF) for solids, ETS-Natural Orbitals for Chemical Valence bond energy decomposition, partial Density Of States (DOS)

XC functionals: (meta) hybrid gradients and NMR, GGA-D for heavy elements, revTPSS

Graphical User Interface: multi-layer support (QM/MM, ONIOM, MOPAC, DFTB, MM)

Other Options: FDE energy, new QUILD version, finite nucleus option, fully relativistic (ZORA+spin-orbit), hybrid-NMR, Faraday constant based on imaginary density approach, Optimized Effective Potential methods

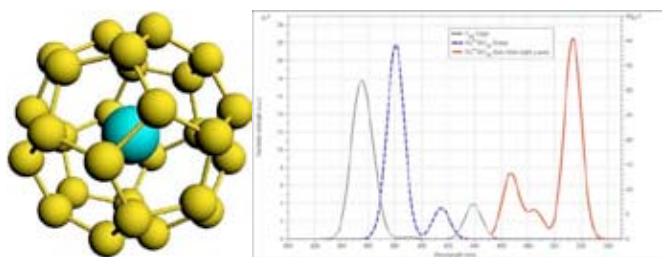
Also Under Development: Mobile Block Hessian, 3D-Reference Interaction Site Model (3D-RISM – a competitor to COSMO), Periodic DFTB, FDE spectroscopy large systems

ADF 2009 preview



Modeling the 32 Electron Rule for Heavy Element Compounds

Inorganic chemists are all familiar with the "18-electron rule" for transition metal complexes. Logically, this leads to a 32-electron rule for inner transition complexes, in which the f orbitals must also play a role. Computational evidence for this rule has recently been set forth by Jean-Pierre Dognon at the Commissariat à l'Énergie Atomique in Saclay, together with Carine Clavaguéra at Ecole Polytechnique (both in France) and Prof. Pekka Pyykkö in Helsinki, Finland. Their results appeared in the January 2009 issue of the [Journal of the American Chemical Society](#) and the February 2007 issue of [Angewandte Chemie International Edition](#). It was also highlighted in the December 15, 2008 issue of [Chemical & Engineering News](#).

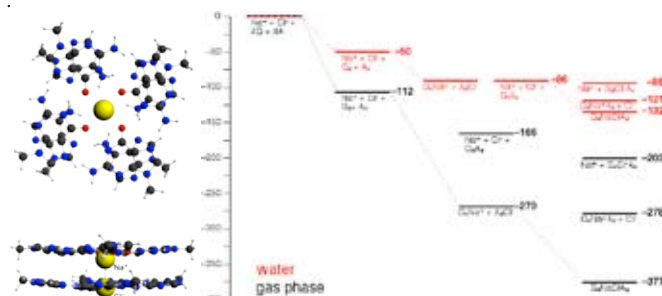


Left: A $\text{Pu}^+@C_{28}$ cluster. Right: UV-Visible spectra, with and without SO coupling.

After a first work on $\text{An}@Pb_{12}$ clusters, the authors modeled energies as well as UV/Vis and IR spectra of several actinide metals encapsulated in C_{28} cages through the use of DFT and TD-DFT. For modeling such compounds with these heavy elements, the relativistic effects implemented through ZORA are quite important, for instance in the spectroscopy of these compounds. Dr. Dognon has also indicated that the bond energy decomposition in ADF, the utility of the ADF GUI for building structures / analyzing results, as well as the good parallelization of the ADF program were all critical to the studies.

Modeling Ditopic ion-pair receptors with ADF and QUILD

While nucleobase quartets are known today for all natural nucleobases and combinations of these, no reports of anion-binding properties of natural nucleobase quartets are known. In a recent communication, Tushar van der Wijst, Célia Fonseca Guerra, Marcel Swart, F. Matthias Bickelhaupt and Bernhard Lippert proposed a potential ditopic ion-pair receptor, based on stacked DNA-base quartets. This work, a collaboration between researchers in Vrije Universiteit Amsterdam, Technische Universitat Dortmund and Instituto Catalana de Recerca i Estudis Avanats Barcelona, appeared in [Angewandte Chemie](#)



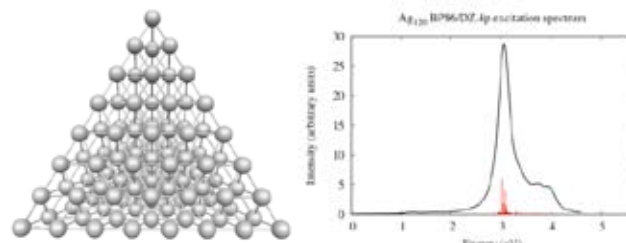
Left: Ditopic receptor G_4NaClA_4 .

Right: Relative energies of complexes.

The puzzling feature of cation binding to an A_4 quartet (A = adenine) via the four exocyclic amino groups in a tetrastranded RNA molecule prompted them to look into the possibility that what was proposed to be a sodium cation in fact might have been an anion. The results of their computational analyses lead to the proposal of the stacking complex of a guanine and an adenine quartet, G_4A_4 , as a potent ditopic receptor for table salt, NaCl, in aqueous solution. Besides the biochemical (structure and stability of telomers in DNA) and potential technological relevance (extracting salt from water) this is also a computational/technical highlight: 8 DNA bases + NaCl (150 atoms), in water, connected through H-bonds, pi-stacking and donor-acceptor bonds. The computations were all carried out with the ADF program, taking advantage of dispersion-corrected DFT-D, which was crucial for the correct treatment of the stacking interactions. The QUILD program, a wrapper around ADF, was employed for its superior geometry optimizer based on adapted delocalized coordinates.

A 120 atom tetrahedral silver cluster modeled with ADF

Professor [Christine Aikens](#) of Kansas State University and Professor [George Schatz](#) of Northwestern University and their co-workers have collaborated on a number of works exploring the electronic spectroscopy of metal nanoparticles with time dependent density functional theory using ADF. A recent report of this work was published in [The Journal of Physical Chemistry C](#), in which they explored the optical absorption properties of silver nano-particles of various sizes.



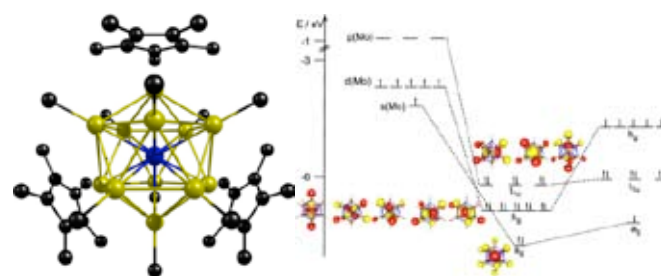
Left: The tetrahedral Ag_{120} cluster.

Right: The excitation spectrum.

Prof. Aikens and her colleagues were able to model such properties for nanoparticles ranging in size from 10 atoms upto the 120 atom tetrahedral nanoparticle depicted above. They were able to carry out such computations in a reasonable amount of time on 4GB compute nodes thanks in part to the fact that ADF takes advantage of the symmetry of molecules, even for TDDFT response calculations. The Aikens group has since extended its exploration of the properties of noble metal nanoparticles to clusters of gold atoms, for which the relativistic effects modeled through ADF's ZORA method are known to be even more important.

The First Dodecahedral Molybdenum Complex studied with ADF

Recently [Prof. Gernot Frenking's group](#) in Marburg, Germany was involved in a joint experimental - theoretical paper that reported the synthesis and characterization of a unique molybdenum - zinc complex in which the zinc atoms coordinate to the central molybdenum in a nearly icosahedral cage. This twelve coordinate structure of zinc atoms about a molybdenum was confirmed in the X-Ray structure depicted below. Their work, published in the October 7, 2008 issue of [Angewandte Chemie](#) was also highlighted in the November 10, 2008 issue of [C&E News](#).



Left: X-Ray Structure of $[MoZn_{12}Me_9Cp^*]_3$.

Right: MO Diagram for $[Mo(ZnH)_{12}]_3$

Coordination complexes with up to nine monodentate ligands have been known for over a century, and also well known are metal - metal clusters, in which one type of metal is entrapped in a shell of surrounding atoms (usually more than nine of them) of another type, with the later metals being electronically bound to one another. One aspect that makes this molecule unique, as revealed by density functional theory calculations with ADF, is its electronic structure. Based in part upon these calculations, the average bond order between the center atom and its ligands was determined to be 1/2, with sd^5 hybrid orbitals on the molybdenum center participating in the covalent bonding with surrounding zinc atoms. Furthermore, the authors determined that an additional six electrons were delocalized amongst the icosahedron formed by the zinc atoms, resulting in weak bonds between them as well. As such, this molybdenum zinc complex appears to have similarities with traditional metal - ligand complexes, with their covalent bonding primarily from the metal to its surrounding ligands, as well as being similar to endohedral metal - metal clusters, characterized by bonding amongst the metal atoms surrounding another.

ADF's [Energy Decomposition Analysis](#) and [Fragment Orbitals](#) were used in this study to obtain a detailed understanding of the electronic structure and bonding of this molecule. According to Prof. Frenking, "the ADF calculations have been crucial for understanding the bonding situation in the molecules because they make it possible to quantitatively estimate the strength of the contributions which come from the s, p and d valence orbitals of the central metal atom."