



The case of orbitals Trond Saue (Toulouse/Oslo)

#### **Some facts**

#### The lanthanide series: Orbital energies



Numerical 4-component atomic Hartree-Fock calculations (GRASP). Average SCF over the  $4f^n5d^16s^2$  configuration.

#### More facts

#### The lanthanide series: radial expectation values



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#### The case



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#### Calculated lanthanide contractions for molecular trihalides and fully hydrated ions: The contributions from relativity and 4f-shell hybridization

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#### Abstract

The calculated lanthanide contraction in the title systems is typically 18–21 pm of which about 9–23% comes from relativistic effects. A pronounced 4f hybridization is found for LuF<sub>3</sub> using three different relativistic methods of calculation. Large lanthanide nuclear quadrupole coupling constants are predicted for the molecular trihalides. © 2006 Elsevier B.V. All rights reserved.

#### The case



Fig. 1. Some scalar-relativistic ZORA/DFT molecular orbitals of LuF3

#### 4. Conclusions

The Lu 4f orbitals are chemically active and mixes with the F(2p) orbitals.

- Hamiltonian: ZORA
- Method: DFT (PBE)
- Basis: QZ4P Slater-type orbitals (22s17p11d6f)

Summarizing, we have provided theoretical values for the lanthanide contraction in realistic molecular systems, demonstrated that relativistic effects account for 9-23%of the total contraction depending on the system, and produced a clear example on 4f participation in chemical bonding.

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# Do f orbitals participate in chemical bonding ????

A leading question !

An answer requires:

- that atomic f orbitals can be identified in the molecule
- that a clear disctinction between chemically active and inactive orbitals can be made



## Probing covalency with X-ray spectroscopy E. I. Solomon, B. Hedman, K. O Hodgson, A. Dey, R. K. Szilagyi,

Coor. Chem. Rev. 249 (2005) 97

- Covalency: "the number of pairs of electrons that a given atom shares with its neighbors" [I. Langmuir, JACS 41 (1919) 868]
- Ligand K-edge XAS has been used to probe covalency in transition metal complexes [B. Hedman, K. O. Hodgson and E. Solomon, JACS 112 (1990) 1643;
   F. Neese, B. Hedman, K. O. Hodgson, and E. I. Solomon, Inorg. Chem. 38 (1999) 4854]



More recently this approach has been extended to f element compounds

# What is an orbital ?

R. S. Mulliken, Phys. Rev. 41(1932) 49; Science 157(1967) 13 **Spectroscopic orbitals:** e.g. canonical (HF) molecular orbitals [CMOs]



Chemical orbitals: e.g. localized orbitals [LMOs]



The HF energy of a closed-shell molecule is invariant to rotations amongst occupied orbitals.

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## **Localization criteria**



 Pipek-Mezey: minimize the number of centers spanning each molecular orbital

$$\mathcal{G}^{\mathcal{P}\mathcal{M}}\left\{\psi_{i}
ight\}=-\sum_{i=1}^{\mathrm{occ}}\sum_{\mathcal{A}=1}^{\mathrm{nuclei}}\left(\mathcal{Q}_{\mathcal{A}}^{i}
ight)^{2}$$

• **Boys:** maximize orbital self-extension (or the distance between orbital charge centroids)

$$G^{B}\left\{\psi_{i}\right\} = \sum_{i=1}^{\operatorname{occ}}\left(\psi_{i}\psi_{i}\left|\left(\mathbf{r}_{1}-\mathbf{r}_{2}\right)^{2}\right|\psi_{i}\psi_{i}\right)$$

Edmiston-Ruedenberg: maximize the electron self-repulsion of each molecular orbital

$$G^{ER}\left\{\psi_{i}\right\} = \sum_{i=1}^{\operatorname{occ}} \left(\psi_{i}\psi_{i}\left|\frac{1}{|\mathbf{r}_{1}-\mathbf{r}_{2}|}\right|\psi_{i}\psi_{i}\right)$$

## From Lewis structures to bonding orbitals



## Carbon dioxide has double bonds, or ?



# Pipek-Mezey localized orbitals of CO<sub>2</sub>

Hund suggested that two-center LMOs correspond to chemical bonds F. Hund, Z. Phys. **73** (1931) 565



Pipek-Mezey localization criterion: 
$$d_i = \left(\sum_{A=1}^{\text{nuclei}} \left(Q_A^i\right)^2\right)^{-1}$$

For each C-O pair the localization procedure gives one  $\sigma$ -bond, two  $\pi$ -bonds and one lone pair !

System	<i>r</i> <sub>C−O</sub> (Å)	Bond energy (kcal/mol)
CO	1.131	257
CO <sub>2</sub>	1.163	192
H <sub>2</sub> CO	1.225	164

#### Resolution of the apparent octet rule violation

T. A. Halgren, L. D. Brown, D. A. Kleier and W. N. Lipscomb, J. Am. Chem. Soc. 99(1977) 6793

$$|\mathbf{O}_{01}| ::: \mathbf{C}_{01}| = |(\operatorname{core})\sigma_{01}^2 \pi_{01x}^2 \pi_{01y}^2 I_{01}^2 \sigma_{02x}^2 \pi_{02x}^2 \pi_{02y}^2 I_{02}^2 |_{02}^2$$

Expansion of LMOs in the ground-state Slater determinant gives determinants that cancel (Pauli principle). The remaining determinants can be regrouped to MO structures, corresponding to the key valence-bond structures, in which the octet rule is not violated.

### Back to our case — LuF<sub>3</sub>

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- Repeating the calculations of Dognon et al. we indeed find considerable mixing of lutetium 4f and ligand 2p orbitals
- Overlaps between fluorine and lutetium atomic orbitals are very small

	$1s_{1/2,1/2}$	$2s_{1/2,1/2}$	$2p_{1/2,1/2}$	$2p_{3/2,1/2}$	2p <sub>3/2,3/2</sub>	
$4f_{5/2,1/2}$	0.000	0.004	0.001	0.004	0.008	
$4f_{5/2,3/2}$	0.001	0.012	0.003	0.006	0.016	
$4f_{5/2,5/2}$	0.002	0.014	0.004	0.014	0.013	
4f <sub>7/2,1/2</sub>	0.001	0.010	0.011	0.011	0.009	
4f <sub>7/2,3/2</sub>	0.002	0.017	0.018	0.004	0.006	
4f <sub>7/2,5/2</sub>	0.000	0.003	0.003	0.005	0.004	
4f <sub>7/2,7/2</sub>	0.002	0.014	0.015	0.016	0.005	
$5d_{3/2,1/2}$	0.022	0.177	0.071	0.095	0.106	
$5d_{3/2,3/2}$	0.011	0.092	0.037	0.047	0.095	
$5d_{5/2,1/2}$	0.023	0.184	0.115	0.105	0.055	
$5d_{5/2,3/2}$	0.020	0.162	0.102	0.090	0.046	
$5d_{5/2,5/2}$	0.007	0.056	0.035	0.086	0.045	
6s <sub>1/2,1/2</sub>	0.025	0.229	0.058	0.038	0.073	
e (LCPQ, Tou	louse)	The	case of orbital			

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#### **Overlap driven vs. degeneracy driven covalency** M. L. Neidig, D. L. Clark, R. L. Martin, Coor. Chem. Rev. 257 (2013) 394

• Consider a two-center molecular orbital

$$\psi = N \left( \phi_M + \lambda \phi_L \right); \quad N = \frac{1}{\sqrt{1 + 2\lambda S_{ML} + \lambda^2}}$$

• Mixing coefficient  $\lambda$  (to lowest order)

$$\lambda = \frac{H_{ML}}{E_M^0 - E_L^0}; \quad H_{ML} \sim S_{ML}$$

- A large mixing coefficient may occur for
  - large numerator: overlap driven covalency
  - small denominator: near-degeneracy driven covalency
- $\bullet\,$  It appears that "bonding" in LuF\_3 is degeneracy driven.
- ...or ?

# Bonding analysis in localized orbitals

Orbital energies obtained as expectation values of the Kohn-Sham matrix

#### • Pipek-Mezey orbitals:

	Orb	$\langle \varepsilon \rangle$	F1	F2	F3	Lu	S	р	d	f
	38	-0.472	0.88	0.00	0.00	0.12	0.03	0.01	0.08	0.01
	42	-0.342	0.90	0.00	0.00	0.10	0.00	0.02	0.06	0.01
•	• Boys orbitals:									
	Orb	$\langle \varepsilon \rangle$	F1	F2	F3	Lu	S	р	d	f
	38	-0.569	0.89	0.00	0.00	0.11	0.02	0.01	0.07	0.01
	42	-0.566	0.95	0.00	0.00	0.05	0.00	0.01	0.03	0.01
	45	-0.566	0.95	0.00	0.00	0.05	0.00	0.01	0.03	0.01
	31	-0.548	0.90	0.00	0.00	0.10	0.01	0.02	0.06	0.01

- No indication of Lu f covalency but
- ...there is no unique definition of localized orbitals !

Is there another way ?

# Our way



#### • Observations:

- In a closed-shell molecule one can freely rotate between the occupied orbitals without changing the total energy; this is the basis for orbital localization.
- If an open-shell is introduced, rotations between closed-shell and open-shell orbitals change the total energy.

#### • Strategy:

- Import 4f orbitals from an atomic calculation into the molecule and keep them frozen during initial optimization.
- ► Make a small fractional hole in the 4f shell (occ. = 14 ϵ) and see if the orbitals stay in this artificial open-shell in the ensuing optimization.

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### Results



The lutentium 4f orbitals do not participate in bonding !

## What can we learn from X-ray spectroscopy ?

- X-ray absorption spectroscopy probes spectroscopic (canonical), not chemical orbitals.
- So what about K-edge XAS ?



#### We rest our case



Sherlock Holmes and Doctor Watson took a tent and went on a camping trip. The first evening after a good meal and a bottle of wine they retired for the night.

During the night Holmes woke Watson and said: I see millions of stars. What does that tell you, Watson?

Watson replied: Astronomically it tells me that there are millions of stars and galaxies and billions of planets. Astrologically is shows that Saturn is in Leo. Theologically I can see God is all powerful and we are small and insignificant. Meteorlogically I believe we will have fine weather tomorrow. What does it tell you, Holmes?

Holmes was silent a moment: Watson, you idiot!. It tells me that somebody has stolen our tent!