Fuzzy atoms and effective atomic orbitals

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What is a molecule?

A system of electrons and nuclei (Physicist picture)

Physical Information:

- Hamiltonian, Wavefunction (density) Hermitian operators (functionals) associated to observables and their expectation values

A system of bonded (interacting) atoms (Chemist picture)

Chemical Information:

- Bonding interaction, steric repulsion, polarity, functional group, aromaticity...

We aim to interpret the results of ab initio calculations in classical chemical terms

The Atom in the Molecule

Atoms are the building blocks of chemistry

- Not observables in Quantum Mechanics.
- Is there a unique atom in molecule (AIM) definition?
- Any AIM is a conceptual construct but with an irrefutable utility.
- Taking advantage of AIM, quantum chemist have defined bond orders indexes, atomic populations, bond orders descriptors, energy partitioning, aromaticity indexes, among others.

Assigning physical quantities to the individual atoms

- Any physical quantity is written as expectation value of one- or two-electron operators
- Which is the physical quantity that can be related to a given chemical concept?

The Atom in the Molecule

- The nucleus is always considered as part of the atom, so the differences always arise in how the physical space (or the Hilbert-space) is subdivided into atomic shares.

- Within the LCAO approach, the atom may be identified with the subspace of the basis functions attached to it. Such approaches are the so-called Hilbert-space analyses.

- A different strategy is to subdivide the physical 3D space into atomic regions or domains, which represent the atom. They may be defined disjoint, like in Bader's "quantum theory of atoms in molecules" (QTAIM), or may be allowed to overlap, like in the different variants of the "fuzzy" atoms

- In Hilbert-space analysis one deals with the AO matrix representation of operators. In 3D-space analysis one usually manipulates density functions

Hilbert-space analysis

Within the MO-LCAO framework, MO are expanded on a finite set of atomic-centered one-electron functions $\{\chi_\mu(\vec{r})\}$ as

$$\varphi_i(\vec{r}) = \sum_\mu c_{\mu i} \chi_\mu(\vec{r})$$

The set of functions centered on a given atom conform an atomic Hilbert subspace $\{\chi_\mu(\vec{r})\}_{\mu \in A}$

In this context, the atom may be defined by its nucleus and the subspace of one-electron basis set centered on it.

A molecular orbital can be rewritten as a sum of its atomic counterparts as

$$\varphi_i(\vec{r}) = \sum_A \sum_{\mu \in A} c_{\mu i} \chi_\mu(\vec{r})$$

Hilbert-space analysis

The electron density can be written as

$$\rho(\vec{r}) = \sum_{\mu\nu} D_{\mu\nu} \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}),$$

where $\mathbf{D}$ is the first-order density matrix in the atomic orbital basis representation. By integrating the density one obtains the total number of electrons

$$N = \int \rho(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} \int \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} S_{\nu\mu} = \sum_\mu (DS)_{\mu\mu},$$

where matrix $\mathbf{S}$ is the atomic **overlap** matrix in AO basis, with elements

$$S_{\nu\mu} = \int \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) d\vec{r}$$

If the underlying AO basis is orthogonal $S_{ij} = \delta_{ij}$ and

$$N = \int \rho(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} \int \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} \delta_{\nu\mu} = \sum_\mu D_{\mu\mu},$$

Hilbert-space analysis

$$N = \int \rho(\vec{r})d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} \int \chi_\nu^*(\vec{r})\chi_\mu(\vec{r})d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} S_{\nu\mu} = \sum_\mu (DS)_{\mu\mu},$$

Mulliken's atomic gross populations N_A

$$N = \sum_A \sum_{\mu\in A} (DS)_{\mu\mu} = \sum_A N_A.$$

Alternatively, one can also write

$$N = \sum_A \sum_B \sum_{\mu\in A} \sum_{\nu\in B} D_{\mu\nu} S_{\nu\mu} = \sum_A N_{AA} + \sum_{A\neq B} N_{AB}$$

where N_{AA} and $N_{AB} + N_{BA}$ are the Mulliken's net and overlap populations, respectively.

Notice that in orthogonal basis there is no overlap population.

Hilbert-space analysis

Pros

- The integrations are analytical for Gaussian functions.
- Straightforward implementation and low computational cost
- The errors associated with any additional numerical integration are avoided.

Cons

- **Basis set dependency**.
- It may show unphysical results for basis sets without marked atomic character e.g. diffuse basis functions.
- Ill-defined in the complete basis set limit (CBS).
- Inapplicable beyond the LCAO-MO approximation e.g. if plane waves are used to expand the MO of the system.

Hilbert-space analysis

Beyond Mulliken Analyses

- Most of the problems associated with Mulliken analyses originate from the overlap of the underlying atomic basis.
- When basis set without marked atomic character are used:
  Overlap populations or bond orders can be negative
  Effective atomic orbitals with occupations not in the $0 \leq \lambda \leq 1$ range

Use of orthogonal basis

The AO basis can be transformed to an orthogonal basis, and the MO expanded into this orthonormalized basis set.

- Symmetric orthogonalization of Lowdin (and a number of variants, see e.g. Comput. Theor. Chem. 1008 (2013) 15)
- Natural orbitals and Natural Population analysis of Weinhold
- Quasi-atomic orbitals of Ruedenberg, etc..

For instance, in Lowdin basis one has

$$\chi_i^L(\vec{r}) = \sum_\mu S_{\mu i}^{-1/2} \chi_\mu(\vec{r}) \qquad \chi_i(\vec{r}) = \sum_\mu S_{\mu i}^{1/2} \chi_\mu^L(\vec{r}) \qquad D_{\mu\nu}^L = (\mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2})_{\mu\nu}$$

$$N = \int \rho(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu} \int \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) d\vec{r} = \sum_{\mu\nu} D_{\mu\nu}^L \delta_{\nu\mu} = \sum_\mu D_{\mu\mu}^L$$

Alternatively, one could also write

$$N = tr(\mathbf{D}\mathbf{S}) = tr(\mathbf{D}\mathbf{S}^{1/2}\mathbf{S}^{1/2}) = tr(\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2}) = \sum_\mu (\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\mu\mu},$$

$$\sum_\mu (\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\mu\mu} = \sum_\mu D_{\mu\mu}^L,$$

Real-space analysis

Disjoint domains

- Voronoi cells
- Quantum Theory of Atoms in Molecules (QTAIM)
- Topological analysis of vector fields other than $\rho(\vec{r})$
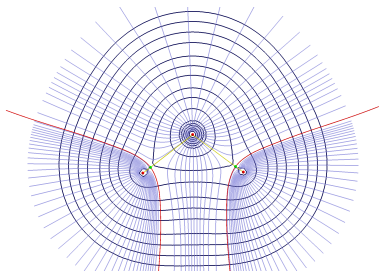
Overlapping domains ("fuzzy" atoms)

- Hirshfeld, Hirshfeld-Iterative, Hirshfeld-X,...
- Becke's constructs, Becke-ρ, TFVC
- Iterative stockholder Atoms (ISA), ISA-X,...

The aim is to decompose the integral of a density function f by performing (numerical) individual integrations over each atomic domain Ω_A

$$\int f(\vec{r}) \, d\vec{r} = \sum_A \int_{\Omega_A} f(\vec{r}) \, d\vec{r}$$

QTAIM

- Topological analysis of $\rho(\vec{r})$
- Atomic basins from the zero-flux condition

$$\nabla \rho(\vec{r}) \cdot \vec{n}(\vec{r}) = \vec{0} \quad \forall \vec{r} \in S(\vec{r})$$

$$\int f(\vec{r}) \, d\vec{r} = \sum_A \int_{\Omega_A} f(\vec{r}) \, d\vec{r}$$

$$\iint f(\vec{r}, \vec{r}') \, d\vec{r} d\vec{r}' = \sum_{AB} \int_{\Omega_A} \int_{\Omega_B} f(\vec{r}, \vec{r}') \, d\vec{r} d\vec{r}'$$

QTAIM

Pros

- Strong physical background (see notes from A.M. Pendás)
- Only information from $\rho(\vec{r})$ is required.

Cons

- Complex shape of the atomic domains leads to cumbersome numerical integrations (but more and more efficients codes are being developed, e.g. AIMAll)
- Spurious non-nuclear attractors (e.g. C_2H_2 with a number of conventional mid-size basis sets) difficult the analysis in chemical terms.

Overlapping domains

One can define a weight function for each atom at each point of the space satisfying

$$w_A(\vec{r}) > 0 \;\; \text{and} \;\; \sum_A w_A(\vec{r}) = 1$$

- Atoms can share the 3D-space (overlap) in general.
- 3D-space partitions makes results virtually basis set independent.
- In QTAIM $w_A(\vec{r}) = 1$ if $\vec{r} \in \Omega_A$ and $w_A(\vec{r}) = 0$ otherwise.

$$\int f(\vec{r}) \, d\vec{r} = \sum_A \int w_A(\vec{r}) f(\vec{r}) \, d\vec{r}$$

$$\iint f(\vec{r}, \vec{r}') \, d\vec{r} d\vec{r}' = \sum_{AB} \iint w_A(\vec{r}) w_B(\vec{r}') f(\vec{r}, \vec{r}') \, d\vec{r} d\vec{r}'$$

Different "fuzzy" atom approaches

Hirshfeld approach, TCA 44 129 (1977).

- Makes use of reference (promolecular) spherically-averaged atomic densities, $\rho_A^0(\vec{r})$
- Superposition of promolecular atomic densities at the actual atomic positions of the molecule defines the promolecular total density , $\rho^0(\vec{r}) = \sum_B \rho_B^0(\vec{r})$
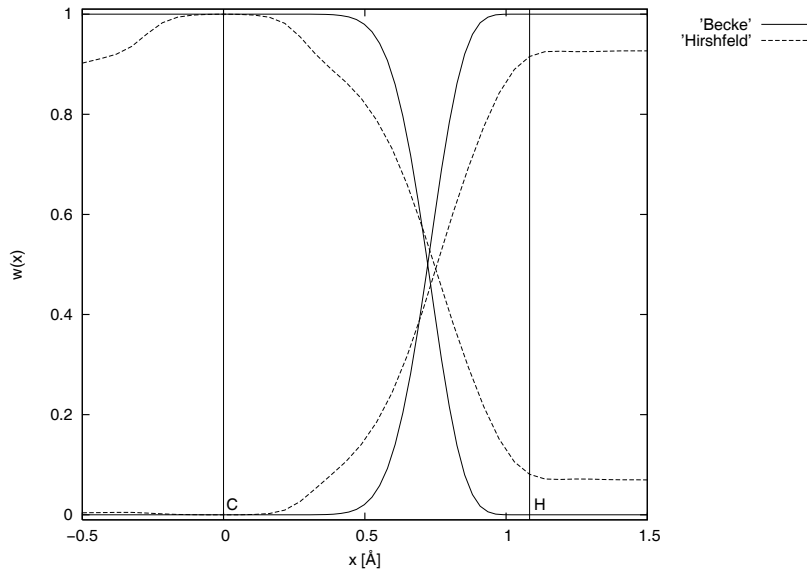
Then, in the classical Hirshfeld method

$$w_A(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_B \rho_B^0(\vec{r})}$$

In recent improvements, $\int \rho_A^0(\vec{r}) d\vec{r} = N_A \neq Z_A$, e.g. Hirshfeld-Iterative, JCP 126 144111 (2007).
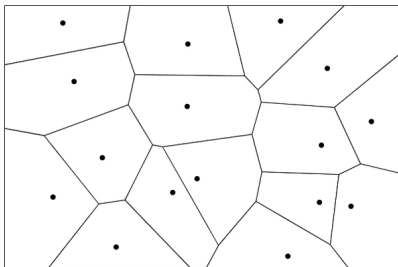
$$\rho_A^{0,N_A}(\vec{r}) = \alpha \rho_A^{0,int(N_A)+1}(\vec{r}) + (1-\alpha)\rho_A^{0,int(N_A)}(\vec{r}), \ \ \alpha = N_A - int(N_A)$$

- Originally devised for effective numerical integration of tree-dimensional functions of marked atomic character.
- Makes use of the so-called Voronoi polyhedra

- The sharp boundaries of the Voronoi cells are substituted by soft functions that ultimately define the atomic weigths
- By construction, $w_A^{becke}(\vec{R}_A) = 1$ and $\partial w_A^{becke}(\vec{r})/\partial(r)|_{r=R_A} = 0$.

Becke's constructs

The scheme can be formulated as follows for the simplest case of a two nuclei system (A and B). For any point of the space one can define the following quantity

$$\mu_{AB} = \frac{r_B - r_A}{R_{AB}}$$

where R_{AB} is the internuclear distance and r_A and r_B represent the distance of that point to nucleus A and B.
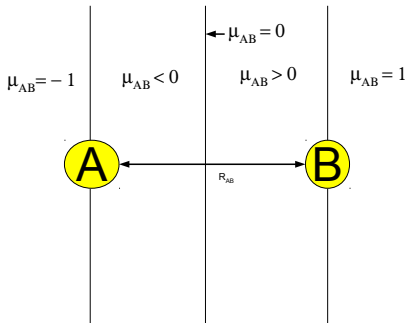
Becke's constructs

The simple step function

$$s_A(\mu_{AB}) = \begin{cases} 1 & -1 \leq \mu_{AB} \leq 0 \\ 0 & 0 < \mu_{AB} \leq 1 \end{cases}$$

can be used to define the sharp Voronoi cell of atom A in this case.

The step function can be replaced by a continuous, monotonically decreasing function in the range [-1,1], and fulfilling the requirements $s(-1)=1$ and $s(+1)=0$ in order to define **fuzzy Voronoi cells**

For that purpose Becke suggested the simple polynomial function

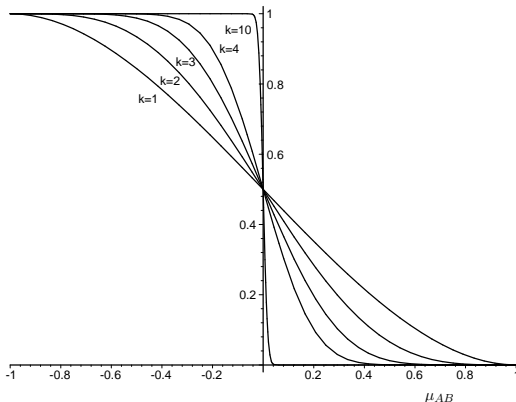$$s_A^k(\mu_{AB}) = \frac{1}{2}[1 - f_k(\mu_{AB})]$$

where

$$f_1(\mu) = \frac{3}{2}\mu - \frac{1}{2}\mu^3$$

Becke's constructs

And devised an iterative process to obtain shaper cutoff profiles

$$f_k(\mu) = f[f_{k-1}(\mu)]$$

The integer k is known as the **stiffness parameter**; the larger the steeper the cutoff profile is.

Becke constructs

In order to account for the different atomic sizes in heteronuclear systems, one can use the same cutoff function but introduce a shifted coordinate. Becke originally uses
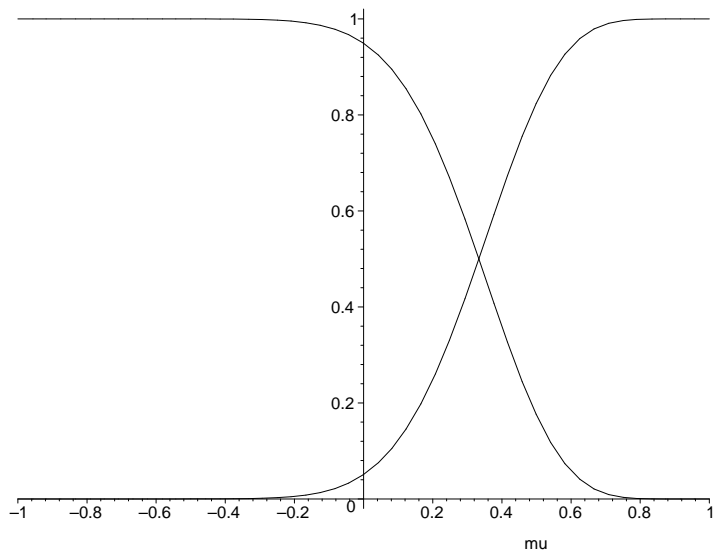
$$\nu_{AB} = \mu_{AB} + a_{AB}(1 - \mu_{AB}^2) \text{ where } \quad a_{AB} = \frac{1 - \chi_{AB}^2}{4\chi_{AB}}$$

$-1/2 \leq a_{AB} \leq 1/2$ to ensure that $0 \leq w_A(\vec{r}) \leq 1$ and $\frac{R_A^0}{R_B^0} = \chi_{AB}$

- For overlapping atoms the position of the interatomic boundaries between all pairs of atoms must be specified.
- A distance criterion is used, namely if $R_{AB} > 2(R_A^0 + R_B^0)$ then $\chi_{AB} = 1$. Otherwise, the atoms are **neighbors** and $\chi_{AB} = \frac{R_A^0}{R_B^0}$

Becke constructs

Cutoff profile for $k = 3$ and $R_A = 2R_B$

Becke constructs

- The set of atomic radii R_A^0 determines the relative size of the atomic Voronoi cells
- The parameter k controls the shape of the cutoff profile.
- Becke used Bragg-Slater radii and k=3 on the basis of more accurate integrations.

Pros

- Numerical integrations in the fuzzy domains are very efficient
- Does not required the use of promolecular atomic densities

Cons

- The use of a fixed atomic radii is a limitation of this AIM model because the same atoms are treated on equal footing in different chemical environments
- Highly arbitrary definition of the atom in the molecule

- Instead of using a set of fixed radii to define χ_{AB} one can use position of the minimum of the density along the internuclear axis connecting two neighbor atoms.
- In Becke's original formula the maximum shift of the interatomic boundary of neighbor atoms occurs when the atomic radii differ by a factor of ca. 2.4
- The set of empirical atomic radii is still invoked for not neighbors
- Distance criterion appears inadequate for intermolecular interactions

Becke and QTAIM

Topological fuzzy Voronoi cells (TFVC)

- The following alternative transformation is monotonic for any value of χ_{AB}.

$$\nu'_{AB} = \frac{1 + \mu_{AB} - \chi_{AB}(1 - \mu_{AB})}{1 + \mu_{AB} + \chi_{AB}(1 - \mu_{AB})}$$

- Two atoms are not considered neighbors if their midpoint is closer to a third atom. Empirical set of radii no longer needed!
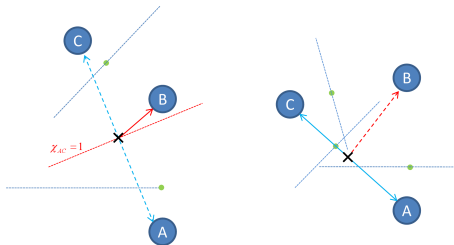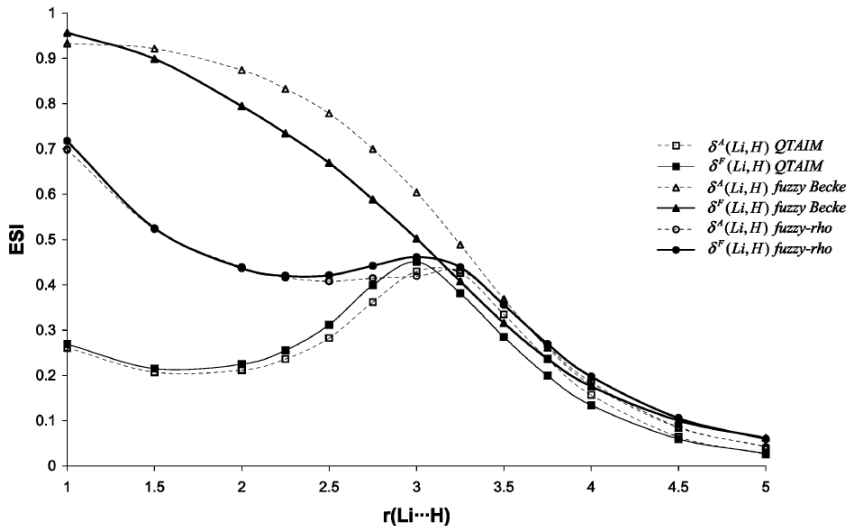
TFVC vs QTAIM

Partial atomic charges for a set of hydrides (LiH to HCl)
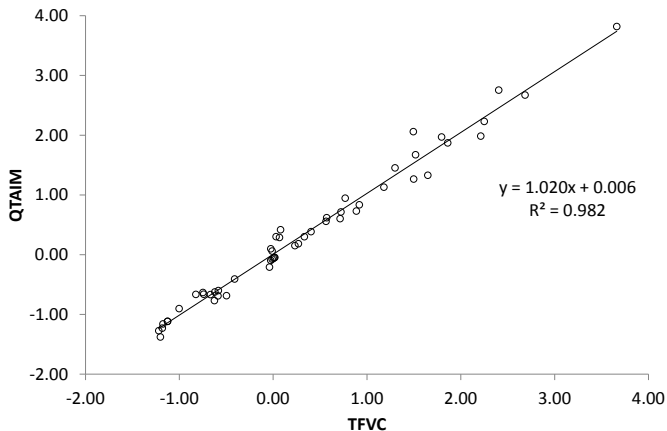
Conditions for proper AIM definitions

- An AIM should be able to account for complex bonding mechanisms (e.g. harpoon effect on LiH)

Conditions for proper AIM definitions

- In aromatic systems, the delocalization index (bond order) should be larger in para- position than in meta-.

Table 7. HF/6-311++G** ESI Values (Meta-ESI and PDI) for Benzene calculated Using Different Atomic Partitions (see text).

	meta-ESI	PDI
QTAIM	0.074	0.098
Becke $k = 3$	0.108	0.101
Becke $k = 4$	0.093	0.101
Becke $k = 5$	0.084	0.102
Becke-rho $k = 3$	0.093	0.092
Becke-rho $k = 4$	0.085	0.094
Becke-rho $k = 5$	0.079	0.095
ISA	0.191	0.122
Hirshfeld	0.192	0.114
Hirshfeld-I	0.203	0.120
Hirshfeld-ID	0.076	0.103

More conditions are necessary...

Effective atomic orbitals:

the atomic orbitals of the topological atom

The effective atomic orbitals

- One very useful tool to characterize the state of the atom within the molecule are the so-called **effective atomic orbitals** (eff-AOs), Mayer JCP 6249 (1996).

- In this approach one obtains **for each atom** a set of orthogonal atomic hybrids and their respective occupation numbers, adding up to the **net** population of the atom.

- These atomic hybrids closely mimic the core and valence shells of the atom, as anticipated on the basis of classical notions of electron configuration of the atom/fragment within the molecule.

$$\rho_{AA}(\vec{r}) = \sum_{\mu} \lambda_{\mu}(w_A(\vec{r})\chi_{\mu}^{A}(\vec{r}))^{*}(w_A(\vec{r})\chi_{\mu}^{A}(\vec{r})) \text{ and } < \chi_i^{A}|\chi_j^{A} >= \delta_{ij}$$

Theory

Let us consider a single-determinant WF formed by n orthonormalized doubly occupied orbitals $\varphi_i(\vec{r})$, $i = 1, 2 \ldots, n$, and a "fuzzy" division of the 3D-space into N_{at} atomic domains Ω_A defined e.g., by a continuous atomic weight function $w_A(\vec{r})$, fulfilling $w_A(\vec{r}) > 0$ and $\sum_A w_A(\vec{r}) = 1$.

Let us for each atom A ($A = 1, 2, \ldots, N_{at}$) form the $n \times n$ Hermitian matrix $\mathbf{Q}^A$ with the elements

$$Q_{ij}^A = \int w_A(\vec{r}) \varphi_i^*(\vec{r}) w_A(\vec{r}) \varphi_j(\vec{r}) d\vec{r}.$$

The matrix $\mathbf{Q}^A$ is essentially the "net atomic overlap matrix" in the basis of the MO-s φ_i. Furthermore, for each atom A we define the "intraatomic" part φ_i^A of every MO φ_i as $w_A(\vec{r}) \varphi_j(\vec{r})$. Thus $Q_{ij}^A = \langle \varphi_i^A | \varphi_j^A \rangle$ i.e., $\mathbf{Q}^A$ is the overlap matrix of the orbitals φ_i^A.

In the case of disjoint domains, $\mathbf{Q}^A$ is also the atomic overlap matrix of the MOs, as $w_a(\vec{r})^2 \equiv w_a(\vec{r})$.

Theory

We diagonalize the Hermitian matrix $\mathbf{Q}^A$ by the unitary matrix $\mathbf{U}^A$:

$$\mathbf{U}^{A\dagger}\mathbf{Q}^A\mathbf{U}^A = \mathbf{\Lambda}^A = diag\{\lambda_i^A\} \quad .$$

It can be shown that every $\lambda_i^A \geq 0$, as is the case for an overlap matrix. The dimension of the matrix also indicates the max. number of non-zero eigenvalues that can be obtained (n), disregarding the size of the underlying set of AOs

For each atom A we can define n_A ($n_A \leq n$) "effective atomic orbitals $\chi_\mu^A(\vec{r})$ as linear combinations of the "intraatomic" parts $\varphi_i^A(\vec{r})$ of the MO-s as

$$\chi_\mu^A(\vec{r}) = \frac{1}{\sqrt{\lambda_\mu^A}} \sum_{i=1}^{n} U_{i\mu}^A \varphi_i^A(\vec{r}) \; ; \qquad \mu = 1, 2, \ldots, n_A \quad ,$$

where n_A is the number of non-zero eigenvalues λ_i^A.

Properties of the eff-AOs

- They are orthonormalized within the atomic domain:

$$\langle \chi_\mu^A | \chi_\nu^A \rangle = \langle \frac{1}{\sqrt{\lambda_\mu^A}} \sum_{i=1}^n U_{i\mu}^A \varphi_i^A | \frac{1}{\sqrt{\lambda_\nu^A}} \sum_{j=1}^n U_{j\nu}^A \varphi_j^A \rangle = \frac{1}{\sqrt{\lambda_\mu^A \lambda_\nu^A}} \sum_{i,j=1}^n (\mathbf{U}^{A\dagger})_{\mu i} Q_{ij}^A U_{j\nu}^A$$

$$= \frac{1}{\sqrt{\lambda_\mu^A \lambda_\nu^A}} \lambda_\mu^A \delta_{\mu\nu} = \delta_{\mu\nu}$$

- The sum of occ. numbers equals the *net* atomic population of the atom

- In the case of disjoint domains (QTAIM), orbitals $\chi_\mu^A(\vec{r})$ differ from zero only in the atomic domain of atom A, thus

$$\langle \chi_\mu^A | \chi_\nu^B \rangle = 0$$

Properties of the eff-AOs

- In the framework of QTAIM they form an orthogonal set of numerical basis functions, and the occ. numbers add up to the atomic populations

- The eff-AOs of atom A can also be obtained **even if no atom-centered basis functions where used in the original MO description**, see CPL 563 97 (2013).

- They can also be obtained in the AO basis from the diagonalization of the matrix $\mathbf{P}\mathbf{S}^A$, where $\mathbf{P}$ is the LCAO density matrix. This alternative permits the straightforward generalization to correlated WFs.

- Alternatively, in the natural orbital representation, the symmetrized form

$$\mathbf{U}'^{A\dagger}\eta^{1/2}\mathbf{Q}^A\eta^{1/2}\mathbf{U}'^A = \mathbf{\Lambda}^A = diag\{\lambda_i^A\}$$

that also produces the same set of eigenvalues, where η is the diagonal matrix of the natural occupations.

The eff-AOs as basis functions

The definition of the eff-AOs can be trivially inverted, and one gets

$$\varphi_j^A(\vec{r}) = \sum_{\mu=1}^{n_A} U_{j\mu}^{A*} \sqrt{\lambda_\mu^A} \chi_\mu^A(\vec{r}) = w_A(\vec{r}) \sum_{\mu=1}^{n_A} U_{j\mu}^{A*} \sqrt{\lambda_\mu^A} \chi(\vec{r})_\mu \quad .$$

Owing to this result, the MO-s can be written as linear combinations of the "effective AO-s" of different atoms:

$$\varphi_i(\vec{r}) = \sum_A^{N_{at}} w_A(\vec{r}) \varphi_i^A(\vec{r}) = \sum_A^{N_{at}} \sum_{\mu=1}^{n_A} U_{i\mu}^{A*} \sqrt{\lambda_\mu^A} \chi_\mu^A(\vec{r}) = \sum_A^{N_{at}} \sum_{\mu=1}^{n_A} c_{\mu i}^A \chi_\mu^A(\vec{r}) \quad .$$

Hilbert-space analysis within QTAIM

The atomic population calculated by Mulliken analysis in the basis of the "effective AO-s" is **equal** to that obtained by the 3D QTAIM analysis.

$$Q_A^{AIM} = \int_{\Omega_A} \rho(\vec{r})dv = 2\int_{\Omega_A} \sum_{i=1}^{n} |\varphi_i(\vec{r})|^2 dv = 2\sum_{i=1}^{n} \int_{\Omega_A} |\varphi_i(\vec{r})|^2 dv = 2\sum_{i=1}^{n} Q_{ii}^A \ .$$

$$Q_A^{LCAO} = \sum_{\nu \in A} D_{\nu\nu} = 2\sum_{i=1}^{n} \sum_{\nu \in A} |C_{\nu i}|^2 = 2\sum_{i=1}^{n} \sum_{\mu=1}^{n_A} \left| U_{i\mu}^{A*} \sqrt{\lambda_\mu} \right|^2 = 2\sum_{i=1}^{n} Q_{ii}^A$$

Analogously, Wiberg bond orders calculated on the basis of eff-AOs are exactly equal to the Delocalization index, and so on.

Similar relationships are also found for fuzzy atomic domains such as TFVC, the only difference being the eff-AOs do not form and orthonormalized set.

Properties

- In practice, the dimension of the eff-AO basis has nothing to do with the dimension of the LCAO basis (if any) used in the original calculations.

- The maximum number of eff-AOs that can be obtained is $N_{at} \times n$, which can be less that the total number of the LCAO basis functions.

- Experience shows that the number of eff-AOs with significant occupation numbers on each atom is limited, and typically much smaller than the number n of the doubly occupied orbitals in the whole molecule.

- The remaining eff-AOs with very small occupation numbers have a marginal significance.

Approximate expressions

One may consider to express the molecular orbitals as a linear combination of an atomic basis set build up from a bf subset of the eff-AOs.

In order to obtain the new LCAO coefficients one can make use of the singular value decomposition (SVD) technique to perform a pairing between the set of eff-AOs from one side, and the set of doubly occupied MO-s from the other.

Let us consider those eff-AO-s χ_μ^A, $A = 1, 2, \dots N_{at}$ which meet some criterion $\lambda_\mu^A \geq t \geq 0$. Let their number be n_{eff}. We build the rectangular $n_{eff} \times n$ matrix $\mathbf{Z}$, with elements

$$Z_{\mu i} = \langle \chi_\mu | \varphi_i \rangle \quad .$$

With the SVD, the rectangular matrix is transformed as

$$\mathbf{U}^\dagger \mathbf{Z} \mathbf{V} = \mathbf{\Xi} \quad ,$$

where $\mathbf{U}$ and $\mathbf{V}$ are unitary matrices of dimension $n_{eff} \times n_{eff}$ and $n \times n$, respectively, and $\mathbf{\Xi}$ is a rectangular diagonal matrix containing the singular values ξ_i of $\mathbf{Z}$.

Approximate expressions

From the definition of matrix $\mathbf{Z}$ one can write

$$\sum_{\mu}^{n_{eff}} \sum_{j}^{n} U_{\mu i}^* \langle \chi_\mu | \varphi_j \rangle V_{ji} = \xi_i \quad ,$$

that is, the singular value ξ_i is the overlap between the function

$$\psi_i = \sum_{\mu=1}^{n_{eff}} U_{\mu i} \chi_\mu \quad ,$$

which is a linear combination of the eff-AOs and

$$\varphi_i' = \sum_{\mu=1}^{n} V_{ji} \varphi_j \quad ,$$

representing a molecular orbital after performing a unitary transformation with the matrix $\mathbf{V}$.

If $\xi_i = 1$ the two functions have an overlap equal one, ψ_i and φ'_i are essentially ("almost everywhere") equal to each other, and one can write

$$\varphi'_i = \sum_{\mu}^{n_{eff}} U_{\mu i} \chi_\mu \quad .$$

That is, the columns of the unitary matrix **U** contain the LCAO coefficients of each rotated MO in the orthogonal basis of eff-AOs.

If ξ_i is close to, but not exactly equal one, this expression represents an approximation to the (rotated) molecular orbital. Under these circumstances the equivalence between the Hilbert-space and real-space populations are no longer strictly fulfilled but, since these approximated MOs form an orthonormalized set, the number of electrons is conserved.
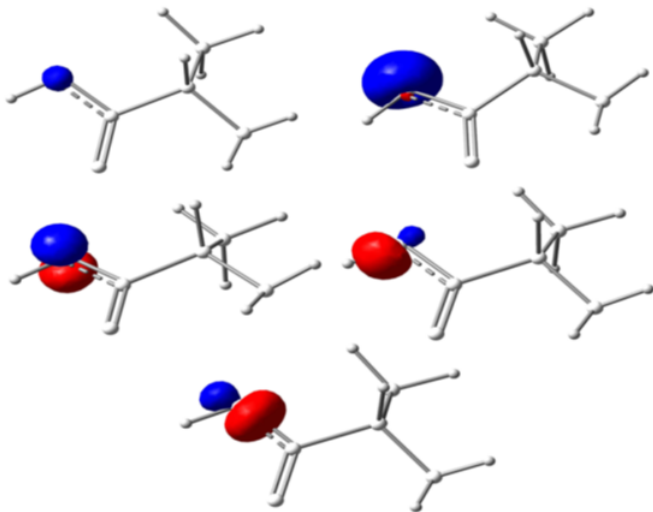
Figure 1: Occupied oxygen eff-AOs in alanine molecule (TFVC)
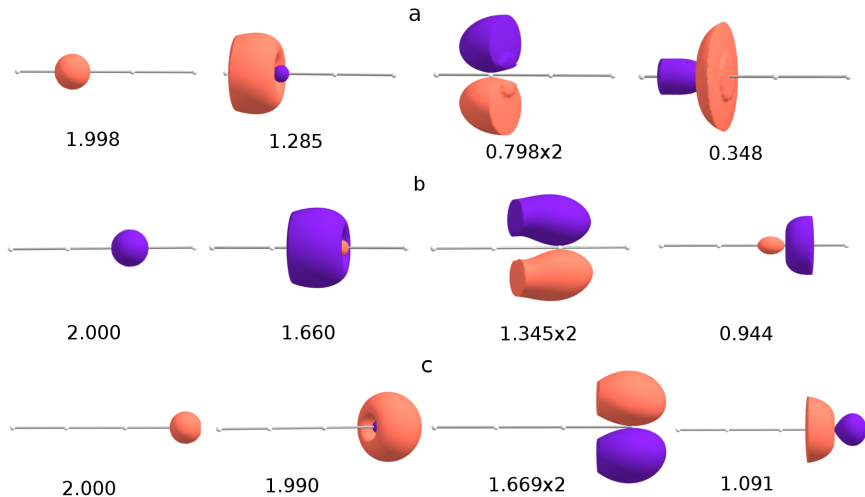
Visualization of the eff-AOs

Figure 2: Highly occupied carbon (a), nitrogen (b), and oxigen (c) orbitals in the HCNO molecule (QTAIM)
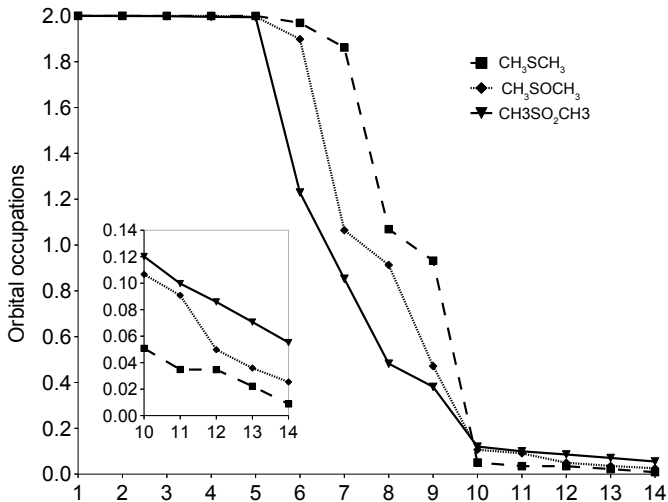
A signature of hypervalency

Figure 3: Occupation numbers of the eff-AOs of S atom on $CH_3S_xCH_3$, x=0,1,2

Formal oxidation states from WF analysis

Formal oxidation states

- The concept of oxidation state (OS) is ubiquitous in transition metal (TM) chemistry and in the study of redox and catalytic reactions.
- Many properties such as reactivity, spin-state, spectroscopic and geometrical features of TM complexes are often rationalized on the basis of the oxidation state of the metal center.
- According to IUPAC, in coordination chemistry, the OS is *the charge left on the metal after all ligands have been removed in their normal, closed shell, configuration*.
- Formal OS are obtained by assigning integer number of electrons to the atoms/ligands according to some rules. In complicated bonding situations involving non-innocent ligands or in intermediates or transition states of catalytic reactions the formal OS assignment may be rather ambiguous.

Conventional population analysis fail

Thom *et al.* illustrated how neither Mulliken charges nor Mulliken spin populations match in general with the oxidation state.

Mulliken (left) and TFVC (right) charges for a set of transition metal complexes.

	Cl^-	H_2O^{HS}	H_2O^{LS}	CN^-	CO	Cl^-	H_2O^{HS}	H_2O^{LS}	CN^-	CO
V^{II}	0.98	1.12	-	0.05	0.64	1.60	1.76	-	1.60	1.64
Mn^{II}	1.10	1.24	1.18	0.10	0.64	1.36	1.64	1.70	1.53	1.53
Mn^{III}	0.93	1.58	1.52	0.35	0.80	1.46	2.05	2.09	1.58	1.67
Fe^{II}	0.86	1.22	1.15	0.01	0.51	1.27	1.63	1.77	1.46	1.44
Fe^{III}	0.99	1.64	1.48	0.24	0.66	1.44	2.06	1.98	1.49	1.58
Ni^{II}	0.99	-	1.08	-0.19	0.31	1.27	-	1.59	1.24	1.30
Zn^{II}	1.02	-	1.06	-0.03	0.52	1.25	-	1.45	1.15	1.19

ab initio determination of oxidation states

- A number or empirical approaches to *correlate* atomic distances or populations with transition metal (TM) oxidation states (bond-valence sum scheme).

- Sit et al.[1] used projection techniques to obtain d orbital populations of central metal in transition metal (TM) complexes. Can not deal with metal-metal bonds.

- Sit et al.[2] also used the positions of the centers of gravity of maximally-localized Wanier Functions. Applicable for plane-waves calculations only.

- Localized Orbital Bond Analysis (LOBA) [3]: MO localization followed by population analysis. A threshold is introduced to distribute electrons among atoms

1. Sit et al., Inorg. Chem. 2011, 50, 10259-10267   2. Sit et al., Chem. Eur. J. 2011, 17, 12136-12143   3. Thom et al., Phys. Chem. Chem. Phys, 2009, 11, 11297

ab initio determination of oxidation states

Focus on the *effective* state of the atoms within the molecule

Derive from the WF some set of "atomic orbitals" and occupation numbers that will allow to assign each electron to a given atom.

Desirable properties of the "atomic orbitals"

- Clear-cut separation (in terms of occupation numbers) of core, valence and virtual orbitals
- Applicable on equal footing for any level of theory and basis set (plane waves, core potentials, etc)
- Basis set independent
- Able to treat alpha and beta electrons independently.
- Able to define functional groups/fragments.

ab initio determination of oxidation states

The eff-AOs, and specially their occupation numbers, can be used to retrieve the appropriate oxidation states of the atoms from the wavefunction from first principles.

Strategy

- Obtain $\rho(\vec{r}, \vec{r}')$ from an *ab initio* calculation.
- For each atom, obtain spin-resolved eff-AOs and occupation numbers up to a given theshold (e.g. 0.1)
- Sort all of them according to decreasing occupation number
- Round the occupation numbers to 1 (i.e. assign occupied eff-AOs) starting from the highest occupied eff-AO until the the number of alpha electrons is reached. Do analogously for the beta part.

Alpha effective atomic orbitals for $Fe(CN)_6^{3-}$ at the B3LYP/6-31G(d) level of theory.

Total number of alpha electrons: 54

Fe		Fe		C		N	
eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup
1s	1.000	3d	0.876	1s	0.996	1s	1.000
2s	1.000	3d	0.848	2s	0.694	2s	0.997
2p	1.000	3d	0.848	2p	0.235	2p	0.728
2p	1.000	3d	0.344	2p	0.232	2p	0.703
2p	1.000	3d	0.314	2p	0.153	2p	0.701
3s	0.991	4s	0.103		0.014		0.020
3p	0.983		0.050		0.013		
3p	0.983		0.050				
3p	0.982		0.049				

Oxidation states for TM complexes

Beta effective atomic orbitals for $Fe(CN)_6^{3-}$ at the B3LYP/6-31G(d) level of theory.

Total number of beta electrons: 53

Fe		Fe		C		N	
eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup
1s	1.000	3d	0.827	1s	0.996	1s	1.000
2s	1.000	3d	0.827	2s	0.708	2s	0.997
2p	1.000	3d	0.305	2p	0.246	2p	0.729
2p	1.000	3d	0.263	2p	0.239	2p	0.702
2p	1.000	3d	0.099	2p	0.153	2p	0.665
3s	0.990	4s	0.049		0.150		0.021
3p	0.982		0.048				
3p	0.982		0.048				
3p	0.982		0.032				

A simple scheme for oxidation states

Oxidation states, last occupied eff-AO (LO) and first unoccupied eff-AO (FU) orbitals for $Fe(CN)_6^{3-}$.

Atom/ Fragment	O.S.	λ^α_{LOEFF}	λ^α_{HUEFF}	λ^β_{LOEFF}	λ^β_{HUEFF}
Fe	+3	0.850	0.344	0.827	0.305
C	+2	0.694	0.235	0.708	0.246
N	-3	0.701	0.020	0.665	0.021

From the "frontier" occupation numbers one can **derive** a simple index R(%) to **quantify** how close is the electron distribution provided by the actual wavefunction to the formal picture of the oxidation states.

$$R(\%) \equiv 100 \, min(1, max(0, \lambda^\sigma_{LO} - \lambda^\sigma_{HU} + 1/2), \text{ for } \sigma = \alpha, \beta.$$

OS for simple transition metal complexes

Table 1: Metal OS and R(%) values for a set of 32 octahedral complexes. HS and LS stand for high-spin and low-spin, respectively.

metal/ligands	Cl^- (HS)	H_2O (HS)	H_2O (LS)	CN^- (LS)	CO (LS)
V^{II}	100	100	-	99	100
Mn^{II}	100	100	100	97	100
Mn^{III}	87	100	100	95	93
Fe^{II}	100	100	100	99	97
Fe^{III}	100	100	100	86	91
Ni^{II}	100	-	100	98	100
Zn^{II}	100	-	100	99	100

The analysis also yielded OS of $(H^{(+)})_2O^{(2-)}$, $C^{(2+)}N^{(3-)}$ and $C^{(2+)}O^{(2-)}$ for the different ligands, conforming with chemical expectations.

Oxidation states for simple molecules

Molecule	O.S.	% trust	q_A/q_B
LiF	$Li^{1+} F^{1-}$	100%	0.83/-0.83
CO	$C^{2+} O^{2-}$	100%	1.13/-1.13
CN^-	$(C^{2+} N^{3-})^{-1}$	97%	0.62/-1.62
NO^+	$(N^{3+} O^{2-})^{+1}$	94%	1.45/-0.45
CO_2	$C^{4+} (O^{2-})_2$	100%	2.23/-1.12
SO_2	$S^{4+} (O^{2-})_2$	100%	2.76/-1.38
SO_3	$S^{6+} (O^{2-})_3$	94%	3.82/-1.27
$HCONH_2$ (formamide)	$H^{1-} C^{4+} O^{2-} N^{3-} (H^{1+})_2$	52%	-0.05/1.67/-1.16 -1.23/0.39
HCNO	$H^{1+} C^{2+} N^{1-} O^{2-}$	60%	0.15/0.95 -0.69/-0.41

Oxidation states for simple molecules

Molecule	O.S.	% trust	q_H
LiH	Li $^{1+}$ H^{1-}	100%	-0.73
BeH$_2$	Be^{2+} (H^{1-})$_2$	100%	-0.66
MgH$_2$	Mg^{2+} (H^{1-})$_2$	100%	-0.63
AlH$_3$	Al^{3+} (H^{1-})$_3$	100%	-0.66
BH$_3$	B^{3+} (H^{1-})$_3$	100%	-0.62
CH$_4$	C^{2+} (H$^{0.5-}$)$_4$	58%	-0.08
SiH$_4$	Si^{4+} (H^{1-})$_4$	100%	-0.67
NH$_3$	N^{3-} (H^{1+})$_3$	81%	+0.30
PH$_3$	P^{3-} (H^{1+})$_3$	100%	-0.69
H$_2$O	(H^{1+})$_2$O^{2-}	100%	+0.56
H$_2$S	(H^{1-})$_2$S^{2+}	55%	-0.21
HF	H^{1+} F^{1-}	100%	+0.72
HCl	H^{1+} Cl^{1-}	78%	+0.18

Oxidation states for simple molecules

Molecule	O.S.	% trust	q_H
B_2H_6	$(B^{3+})_2(H^{1-})_6$	100%	-0.60/-0.67
C_2H_6	$(C^{2+})_2(H^{0.66-})_6$	63%	-0.10
C_2H_4	$(C^{2+})_2(H^{1-})_4$	52%	-0.05
C_6H_6	$(C^{1+})_6(H^{1-})_6$	54%	-0.06
C_2H_2	$(C^{1-})_2(H^{1+})_2$	57%	+0.09

Limit of applicability

- Large ambiguity in the OS of hydrocarbons (and possibly for other systems exhibiting bonds with extremely weak polarity)
- Large systems in general (definition of fragments/functional groups is necessary)

A hierarchical scheme for oxidation states

- Define atoms/fragments/ligands of the system

$$w_{\Gamma_i}(\vec{r}) \equiv \sum_{A \in \Gamma_i} w_A(\vec{r}) \qquad \mathbf{S}^{\Gamma_i} \neq \sum_{A \in \Gamma_i} \mathbf{S}^A$$

- Obtain spin resolved eff-AOs for all Γ_i fragments
- Distribute the number of electrons among the fragments according to occupations of their eff-AOs
- Get most appropriate atom/ligand oxidation states and R(%) index.
- If necessary, the OS for the atoms of a given fragment can be subsequently obtained by obtaining the eff-AOs for every atom and distributing the number of alpha and beta electrons that were assigned to the ligand in the previous step.

Active species of the catalytic hydroxylation with Fe(Pytacn) complex
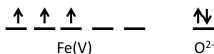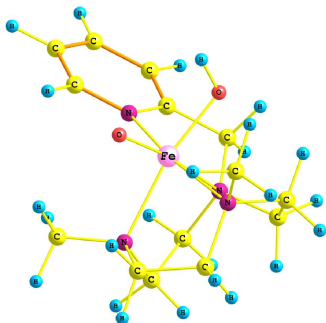
Fragment	O.S.	ALPHA		BETA		Atomic spin densities
		λ_{LOEFF}	λ_{HUEFF}	λ_{LOEFF}	λ_{HUEFF}	
Fe	+5	0.94	0.50	0.99	0.46	2.10
OH	-1	0.69	<0.05	0.77	<0.05	0.12
O	-2	0.64	<0.05	0.46	<0.05	0.85
Ptacyn	0	0.55	<0.05	0.71	<0.05	

$Sc_2C_2@C_{80}$ IPR5

Sc_2C_2

Cage Charge	C(%)
-4	100%

Atom/ Fragment	Oxidation state
Sc	3+
C_2	2-

C(%) = 100%

$Sc_4O_2@C_{80}$ I_h

Sc_4O_2

Atom/Fragment	Oxidation state
Sc_{eq}	3+
Sc_{ax}	2+
O	2-

C(%) = 60%

Cage Charge	C(%)
-6	100%

Endohedral fullerenes

$Sc_4C_2@C_{80}$
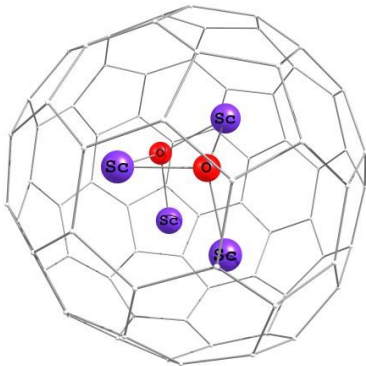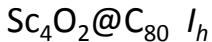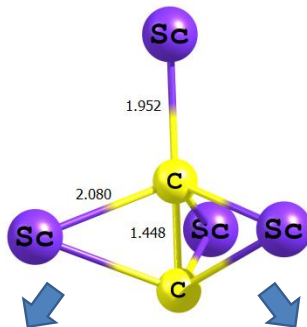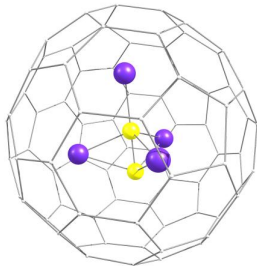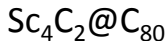
Cage Charge	C(%)
-6	100%

Atom/ Fragment	OS
Sc	3+
C_2	6-

$\lambda_{LOEFF} (C_2) = 0.392$

C(%) = 68%

Atom/ Fragment	OS
Sc	3+
C	4-
C	2-

C(%) = 62%