The Local Properties of the Electronic Structure

A Bridge between Theory and Experiment

Valera Veryazov

`Valera.Veryazov@teokem.lu.se`
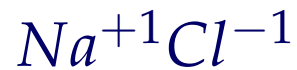
Department of Theoretical Chemistry

Lund University

Atomic Valency in chemistry textbooks

$NaCl$
table salt

$KClO_3$
Berthollet's salt

$Na^{+1}Cl^{-1}$
$Na^{I}Cl^{I}$

$K^{+1}(ClO_3)^{-1}$
$K^{I}Cl^{V}O_3^{II}$

The rule: *Use stoichiometry and bond counting!*

Drawbacks of 'arithmetic' approach

Stoichiometry:

- valency should change under bond breaking or bond formation.
- obviously fails for systems with bonds between same element: organic molecules, allotropes

Bond counting:

- ignores bond lengths

- can be used only in covalent systems: crystalline $NaCl$: 6 neighbours, $CsCl$: 8.

- how count bonds in molecules with Van der Waals bonds, dimers, carbonyls?

Can quantum mechanics help?

The expectation value of an operator:
$$\langle \hat{\Omega} \rangle = \int \psi^* \hat{\Omega} \psi d\tau = \langle \psi | \hat{\Omega} | \psi \rangle$$

Examples of observables: energy, dipole moment.

Atomic charge, valency are not observable!
we MUST rely on the chemical sense to obtain them
as an interpretation of the results.

To answer "Can we use $NaCl$ instead of $KClO_3$?"
one has to study reactions...

Outline

- methods to compute atomic valency
- introduction to density matrix formalism
- local properties of electronic structure
- practical examples

Methods to compute valency

- improved bond counting
  - ♦ valency index

- geometry related counting of electrons
  - ♦ atom-in-molecule

- density matrix analysis
  - ♦ various atomic charges
  - ♦ bond orders and covalency
  - ♦ full valency

Valency index

Buckingham potential: $\Phi_{12}(r) = A\,exp(-Br) - C/r^6$
Used as a pair potential in ionic systems.

Valency index by I.D.Brown:

1. select trusted crystal structures with known atomic valencies
2. calibrate A, B and C to reproduce atomic valencies (instead of energy)
3. verify on unknown structures

Result: (in 1985) about 10% of crystal structures in ICSD database have atoms with "strange" atomic valencies.
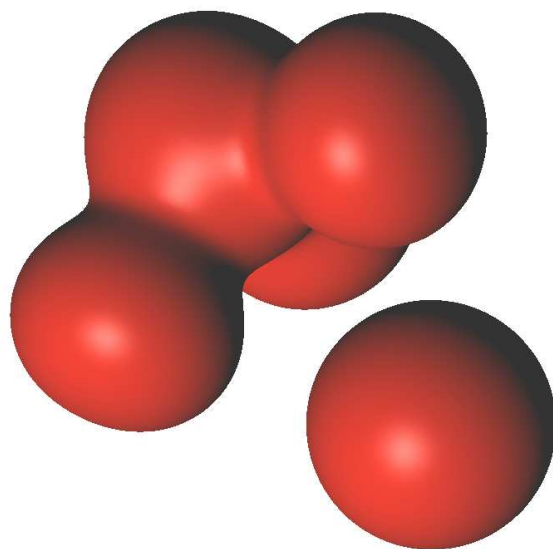Or, they have "strange" interatomic distances.

Atom-in-molecule

Quantum chemistry can compute electron density as a function of coordinates.
$KClO_3$ density computed by Hartree-Fock method:

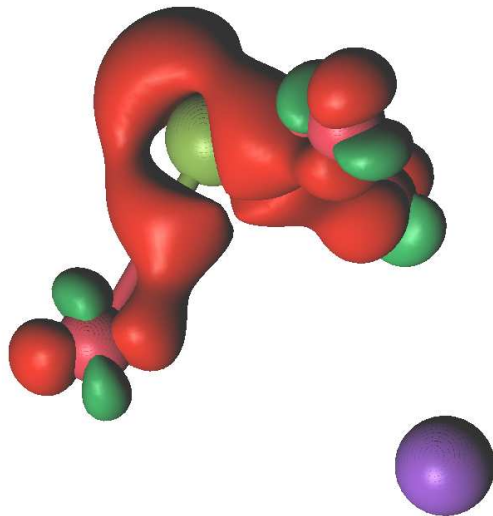File:kclo3.grid MO:Density Level:0.040
Subspaces: i:30; s:27;

The problem: how to separate atoms and bonds?

Geometry based separation of atoms

$KClO_3$ density minus 'individual ions' density:

File:res.grid MO:Density Level:0.040

K is almost a cation, O and Cl are too mixed in space.
Bader analysis: zero flux surfaces.

Electrostatic potential charges

We can vary point charges on atoms, in order to reproduce (in least-squares mean) the computed density (in the set of points, e.g. in a grid).

For molecules with small amount of atoms, extra centers with atomic charge should be used.

main problem: low transferability among similar molecules

Density matrix

Density matrix is the result of any quantum chemical calculation: Hartree-Fock, DFT, multiconfigurational, etc.
$D_{\mu\nu} = \sum_i \theta_i C_{\mu i} C_{\nu i}^*$, where θ is an occupation for orbital i.

We can construct population matrix P,
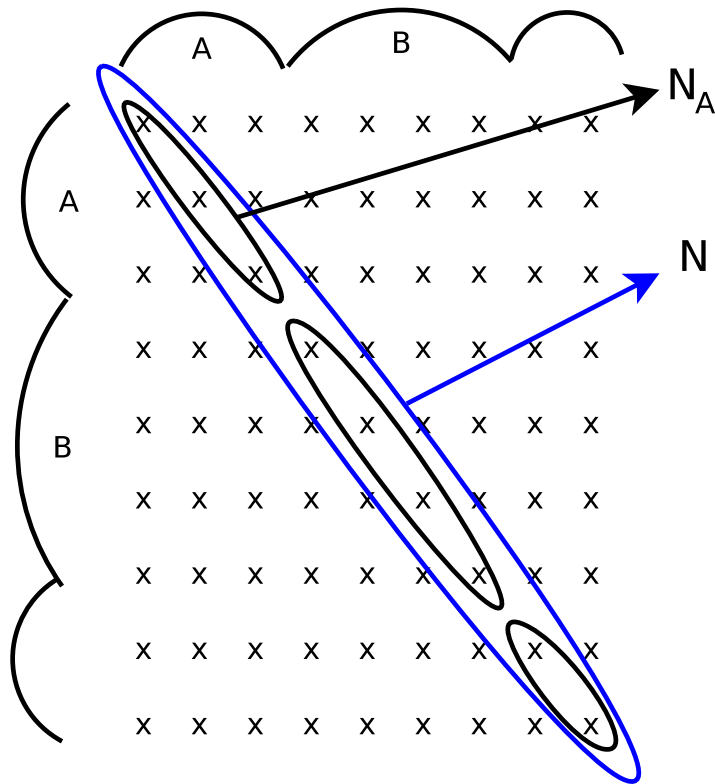as a product of density matrix and overlap matrix.
$P_{\mu\nu} = (DS)_{\mu\nu}$

Trace of P is the number of electrons: $\sum_{\mu} P_{\mu\mu} = N$

Population matrix

Now we can split P into atomic blocks ($\mu \in A$)
and assosiate N_A with an atom.
For non-atomic basis set we make a projection first.

Population analysis

Density matrix and population matrix are invariant to unitary transformation, but N_A are not.

- Mulliken charges (*R. Mulliken, 1955*)

- Löwdin charges (*P-O. Löwdin, 1955*) (orthogonalized by $S^{1/2}$)

- Natural Bond Order (NBO) (*F. Weinhold, 1983*) (orthogonalized with constrained occupations)

- Loprop charges (*G.Karlström, 2004*) (separate orthogonalization for occupied and virtuals)
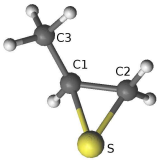
- .

Why do we need that many?

If we take *NaCl* molecule, same method (HF),
but different basis sets:
from minimal to extended (independently).
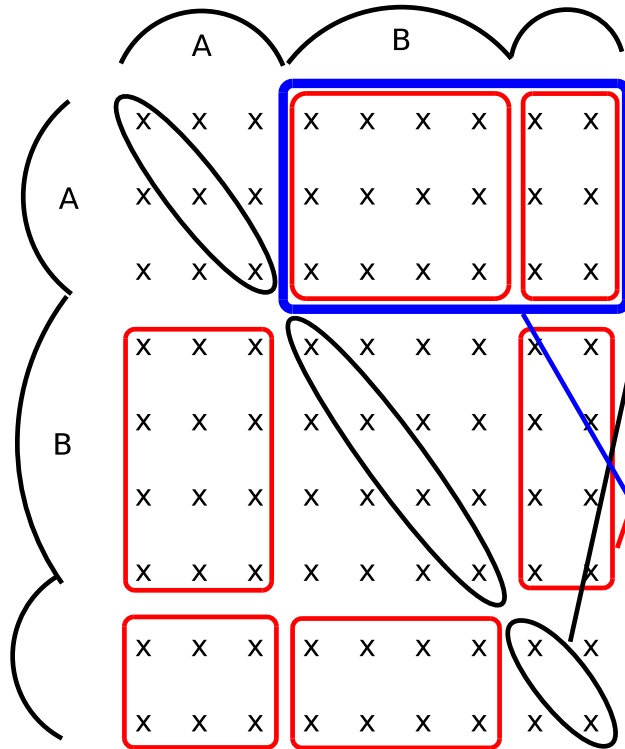Mulliken charges vary from 0.58 to 0.96
Loprop charges vary from 0.85 to 0.89

Methyl ethylene sulfide:

	Mulliken	NBO	Loprop	ESP
C(H2)	-0.52	-0.56	-0.24	-0.34
C(H)	-0.41	-0.37	-0.07	0.04
S	0.07	0.11	-0.09	-0.19
C(H3)	-0.57	-0.67	-0.33	-0.30

Local properties from density matrix

$$N_A = \sum_{a \in A} P_{aa}$$

$$Q_A = Z_A - N_A$$

$$W_{AB} = \sum_{a \in A, b \in B} P_{ab} P_{ba}$$

(K. Wiberg, 1968)

$$C_A = \sum_{B \neq A} W_{AB}$$

(D.R. Armstrong, 1973)

mixing ionic and covalent

in ionic case: $|Q_A| \simeq valency$
in covalent case: $C_A \simeq valency$

H_2O	Q_A	C_A
H	0.33	0.88
O	-0.66	1.73

$NaCl$	Q_A	C_A
Na	0.88	0.54
Cl	-0.88	0.54

$KClO_3$	Q_A	C_A
K	0.89	0.03
Cl	1.78	4.05
O	-0.89	1.42

Full atomic valency

How to combine two opposite cases: covalent and ionic?
A magic formula:

$$V_A = \tfrac{1}{2}\left(C_A + \sqrt{C_A^2 + 4Q_A^2}\right) \qquad (V.Veryazov, 1991)$$

- $V_A \simeq |Q_A| + \tfrac{1}{2}C_A$, if C_A is small
  take fully transferred electrons and add half of covalent pairs.

- $V_A \simeq C_A$, if $|Q_A|$ is small

But, does it work better?

Sometime it does!

H_2O	Q_A	C_A	V_A
H	0.33	0.88	1.00
O	-0.66	1.73	1.97

$NaCl$	Q_A	C_A	V_A
Na	0.88	0.54	1.03
Cl	-0.88	0.54	1.03

$KClO_3$	Q_A	C_A	V_A
K	0.89	0.03	0.91
Cl	1.78	4.05	4.72
O	-0.89	1.42	1.84

How to improve the definition?

Problems:

- calculations have to be performed with good quality basis set
  But interpretation results are more stable with compact basis sets

- description of the covalent bond:
  high bond orders are less reliable

- description of delocalized metallic bond

How to treat discrepancies?

Making a new formula for computed atomic valency
we want to match the expected value.
But what if we get 2.3, or 2.7 instead of 2?

- is it a new valency state?

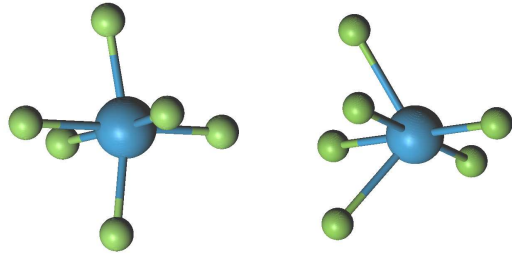- is it a defect of calculation?

- is it a defect of interpretation?

Mixed valency

Pb_2O_3 crystal
Space group=$P2_1/a$, Z=4
two kinds of Pb, both 6-coordinated by O

Interatomic distances:
2.08 2.14 2.16 2.17 2.26 2.28 Å
2.31 2.43 2.44 2.64 2.91 3.00 Å
Do we have Pb^{III} or mixture Pb^{II} and Pb^{IV}?

Full valency results: 2.32 and 3.94

The importance of correct density

What happens with $NaCl$ molecule during dissociation?

Hartree-Fock and DFT theory give ionic solution,
so, full valency will never become 0.

In multiconfigurational approach, e.g. CASSCF,
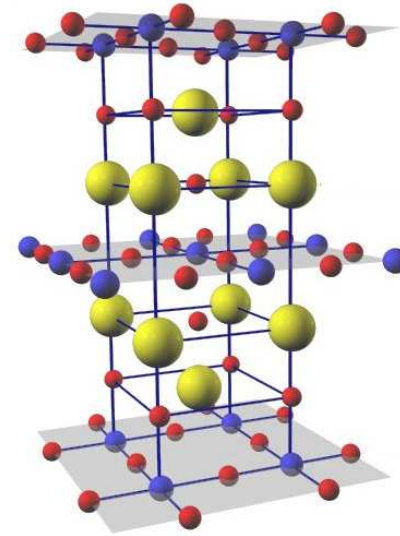full valency of atoms goes from 1 to 0.

Non stoichiometric compounds

HTSC materials:
La_2CuO_{4+x}, $YBa_2Cu_3O_{7-x}$
The formal valency of Cu
is higher than 2,
but is it Cu^{III} or O^I?

Strong correlation effects influence the result of
density calculations.
Interpretation (charges, valency) varies dramatically
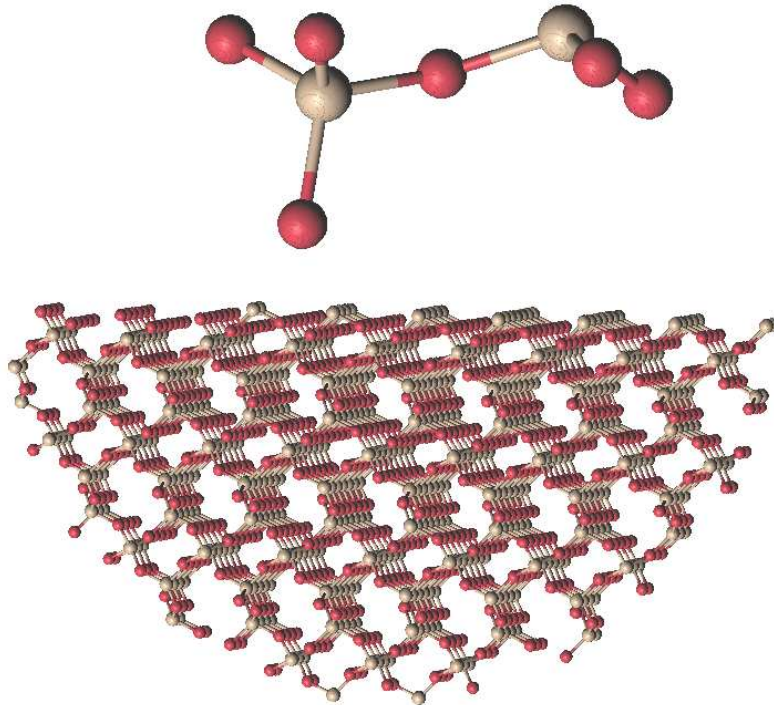
Surface relaxation

How to estimate a stability of a surface?
Solution 1: compute all possible displacements,
study saturation of broken bonds.
Solution 2: compare valency in the bulk (unperturbed) and
on the surface.

Conclusion: the local properties form an easy and convenient language to describe the electronic structure, and thus connect the theoretical description and observable reality.

Thank you!