### (Resonating) Valence Bonds: Lost Tribe(s) of Solid-State Quantum Chemistry.

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The concept of (chemical) bonding is widely spread, but it is rarely realized that in fact it is based on very archetypical features of human thinking which may manifest in very different formal disguises remaining substantially unchanged. In the first part of this talk I am going to give some kind of historical perspective of the genesis of the idea of chemical bond and demonstrate how this concept may be (and actually had been many times) used for developing not that much known quantum chemistry methods explicitly employing the idea of bonding. Next, the limitations of the concept of the isolated chemical bond well known in (quantum) chemistry will be highlighted and two recipes known to handle these restrictions will be confronted (molecular orbitals - MO vs (resonating) valence bonds -(R)VB). Finally, the implications of the RVB hypothesis for a specific solid state problem (CuNCN physics) will be presented.

Very remarkably, the RVB states cannot be reproduced by any available solid state quantum chemistry software which is absolutely and alternativelessly dominated by the Hartree-Fock approximation. The very possibility of the RVB ground state is not programmed, which makes it elusive due to this restriction of the software. The situation is in a way scandalous in a view of importance of the RVB states for the high- $T_c$  behavior, but also due to its possible wider occurrence in practice as proven by our CuNCN experience.

### Once upon a time...





### Once upon a time...



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et quamvis subito per colum vina videmus perfluere, at contra tardum cunctatur olivom, aut quia ni mirum maioribus est elementis aut magis hamatis inter se perque plicatis, atque ideo fit uti non tam diducta repente inter se possint primordia singula quaeque

wine runs easily, oil slowly through a strainer, because the elements of oil are larger or more hooked, and so cannot separate so readily.

### Nature and nature's laws lay hid in night; God said "Let Newton be" and all was light.



Field...

\*

undirectional, unsaturable...

### ... but it did not work...J. Proust



\*Atoms combine in specific proportions so like each of them had an integer number of hooks specific for each element... \*At this point the classical (Newtonian) picture of the Universe had been seriously questioned at the first time...

### Edward Frankland: 1852. Valence...



Fixed valence characteristic for each given chemical element as an integer number... of hooks?.. Carbon (C) has four hooks?, hydrogen (H) – one; oxygen (O) – two, etc...

### Boutleroff: chemical structure theory



«Assuming that only a definite and restricted (limited ?) amount of chemical force (affinity) belongs to each chemical atom, with which it takes part in forming of a body, I would call *chemical structure* that chemical bond or a way of mutual connection of atoms in a composite body....»



### ... consider a simpler example: C<sub>2</sub>H<sub>6</sub>O

### \*C<sub>2</sub>H<sub>5</sub>OH



### \*CH<sub>3</sub>OCH<sub>3</sub>



### ... but also magyifica hardiferences...





## Naïve (sorry, physical) approach is: to write a Hamiltonian... : $H = \frac{1}{2} \sum_{\alpha}^{\alpha} \frac{1}{M_{\alpha}} \Delta_{\alpha} + \frac{1}{2m} \sum_{i}^{\alpha} \Delta_{i} + \frac{1}$ $+\frac{1}{2}\sum_{\alpha}^{A}\frac{Z_{\alpha}Z_{\beta}}{|\vec{R}_{\alpha}-\vec{R}_{\beta}|}+\frac{1}{2}\sum_{i}^{N}\frac{1}{|\vec{r}_{i}-\vec{r}_{j}|}-\sum_{\alpha}^{AN}\frac{Z_{\alpha}}{|\vec{R}_{\alpha}-\vec{r}_{i}|}$

... and to recognize that one for  $C_2H_5OH$  and  $CH_3OCH_3$  is the same. Amazing... Where the difference can come from ?

### ... Chemists know the answer, but they largely do not know that (and what) they know ...



### In the organic chemistry realm topology provides extremely efficient means for naming...



## ... describing, and predicting (also reactivity)



It works without explicit reference to what are these sticks

### Next approach: Alexejeff & Gordan: 1900



Wissarion Grigorjewitsch Alexejeff



Paul Albert Gordan: (Clebsch-Gordan).

### What did Alexejeff do?

No more no less: Invented valence bond wave function without knowing what is wave function, what is electron, what is whatsoever. Represented chemical transformations with operations with functions

Die Formeln, wie sie bis jetzt in der Chemie gangbar waren: HHH Ħ Propylalkohol, (C.H.O) Kaliumglykolat, (C.H.O.K). Ħ Tertiärer Butylalkohol, (C.H., O). Amidothiacetsaure, (C.H.O.SN). CHa H CH. HC HC CHParadichlorbenzol, (p.C.H.Cla) Orthodimethylbenzol (o-C.H.e).

 $C = c_x c_x c_x c_x = c_x^4, \quad H = h_x, \quad O = o_x o_x = o_{x_i}^2, \quad Cl = cl_x$ Kohlenstoff Wasserstoff Sauerstoff Chlor  $K = k_x \text{ Kalium, } N = n_x n_x n_x = n_x^3 \text{ Stickstoff u. s. w.}$ 

Unsere obigen Formeln nehmen in der neuen Bezeichnung folgende Form an:

> $(c_1c_2)(c_2c_3)(c_1h)^3(c_2h)^2(c_3h)^2(c_3o)(oh)$ Primärer Propylalkohol,

 $\begin{array}{c} (c_1c_3)(c_1h)^2(c_1o)(oh)(c_2o_1)^2(c_3o_3)(o_2k)\\ {\rm Kaliumglykolat,} \end{array}$ 

 $(c_1c_2)(c_1h)^2(c_1n)(nh)^2(c_2o)^2(c_2o_1)(o_1s)(sh)$ Amidothiacetsäure,

 $\begin{array}{c} (c_1c_2)(c_1c_3)(c_1c_4)(c_3h)^3(c_3h)^3(c_4h)^3(c_1o)(ah)\\ \\ \text{Tertiārer Butylalkohol,} \end{array}$ 

 $\begin{array}{c} (c_1c_2)(c_3c_3)^2(c_3c_4)(c_4c_5)^2(c_5c_6)(c_6c_1)^2(c_1c)(ch)^3(c_2\bar{c})(\bar{c}h)^3(c_3h)(c_4h)(c_5h)(c_6h)\\ \text{Orthodimethylbenzol.} \end{array}$ 

### Thus: Alexejeff & Gordan

\*labelled chemical structure formulae by functions... of a very special kind;

\*The (*a*,*b*) symbols stand for a determinant of coordinates of 2-dimensional vectors *a* and *b*:

 $(a,b) = a_x b_y - b_x a_y.$ 

\*Moreover: mathematical operations have been discovered which describe redistribution of sticks/bonds...
\*And this all without slightest reference to electrons...



Lewis suggested shared electron pairs to be responsible for bonding. That is (unpaired) electrons are the hooks...

### What did London, Heitler, Weyl & Rumer do?

\*Established the bonding wave function of H<sub>2</sub>; \*Identified the (*a*,*b*) multipliers in the Gordan-Alexejeff construct as electron spin-invariants – determinants of the spin-1/2 components... singlets...

\*Based on newly established *physical* nature of the

*structure formulae* as of the *electronic wave function* wrote the *energy* expression corresponding to a *structure formula*.

\*That covered "almost" all organic chemistry...

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н

- Н н н н н н Н H
- Н н H Н н н н Н Н

- **Obvious advantages of** VB:
  - $\circ$  Inherent O(N)
  - Correct asymptotic
  - Transferable bonds
- **Minor problem:** 
  - Unclear what orbitals form bonds...

a slide made for physicists/mathematicians... ... chemists know this all, but they largely do not know what they know ...

### $C_2H_5OH = C_2H_6O = CH_3OCH_3$



### ... so we enter into play and address right the minor problem



... that of determination of the orbitals forming bonds (and not only bonds) from variation principle ...

... and arrived to the series of SLG methods featuring the O(N) scaling on physical grounds...





- But the history took other, MO path:
   Inherent O(N<sup>3</sup>)
   Wrong asymptotic
   Nontransferable MO's
- And not while people were stupid...



Respectively, by Claus (1867), Dewar (1867), Ladenburg (1869), Armstrong (1887), Thiele (1899) and Kekulé (1865). Dewar benzene and <u>prismane</u> (Ladenburg benzene) are different chemicals that indeed have Dewar's and Ladenburg's structures. Thiele and Kekulé's structures are used today.

### Benzene: Kekulé's ad hoc solution...



oder kurz:



Already Kekulé himself had been convinced through his discussions with Ladenburg that a model with three double and three single bonds is not good. So he finally said that it oscillates between these two structures... whatever it means...

### Berichte der durstigen Chemischen Gesellschaft



\*Unerhörter Jahrgang, Nr. 20 zum 20.9.1886 "Sitzung vom 20. September 1886. Vorsitzender: Hr. August Kuleké, Präsident."

### What is Rumer famous for? In fact, for the RVB wave function...



Some people believe, it was invented by P.W. Anderson... But both Kekulé and Rumer also had something to say...

$$\Psi_{RVB} = \sum_{\{r,r'\}} \prod_{r,r'} \frac{1}{\sqrt{2}} (c_{r_{\uparrow}}^{+} c_{r_{\downarrow}}^{+} + c_{r_{\downarrow}}^{+} c_{r_{\uparrow}}^{+})$$

### L. Pauling was so inspired that some people now believe, it was he, who invented it ...





## But... E. Hückel proposed another representation of benzene $\pi$ -electrons





### a different picture





... in chemistry books one frequently reads something like 'since in benzene  $\pi$ -system bonds are non-localizable and a resonance takes place it is advisable / convenient / reasonable to introduce delocalized description of this system and to use a picture as proposed by Hückel: construct the WF of the occupied delocalized MOs.'

Is it true?..

### if one compares ...



\*Rumer and Hückel suggested definitely not the same function...

#### moreover...



\*It cannot be a coincidence...

### The remaining 75% are equally distributed among the singly and doubly ionic configurations ...



the total weight  $w_k$  of the *k*-ionic configurations in the HF solution of a cycle with 2n nodes each with one orbital is:

$$w_k \rightarrow \binom{n}{k} 2^{-n}; w_k = w_{n-k},$$

apparently

$$w_0 \to 0 \text{ if } n \to \infty$$

that is, in a crystal...

The BS solution is only slightly better; for benzene:  $\Psi_{BS} = \Psi_{N\acute{e}el} = |1_{\uparrow}2_{\downarrow}3_{\uparrow}4_{\downarrow}5_{\uparrow}6_{\downarrow}|$ has no definite total spin, and the longer the chain is, the

less is the contribution of the singlet...

### VB vs MO Theory: A Never-Ending Rivalry?

- \*The results of VB and MO are the same in "infinity"... ③ If a full set of basis states is used, it does not matter which one is taken as a "first" one...
- \*but we live here and now, not in "infinity", so it is a
- legitimate and important question, how to make a finite expansion shorter?... In different situations either VB or MO may be a good starting point or a good approximation to the "correct" answer...
- \* Basically they have nothing to do with each other: I would say it's more than a rivalry...
- \*Most important: the solid state quantum chemistry software is *all* inherently MO-(Hückel) based

## What is available in the solid state context?

\**All* solid state quantum chemistry software is inherently based on the Hückel *resp.* Hartree-Fock wave function... - uses Bloch sums of AO's... and yields delocalized: Bloch states resp., MO's... \*Some modifications of Hamiltonian (+U) ... \*Brocken symmetry solutions (BSS) ...

\*... But

\*Changing Hamiltonian does not rectify the wave function;
\* BSS leads to magnetically ordered states;
\*Although the overlap with the correct solution will be probably better,

the BSS are **not** states of definite total spin...

\*btw, there is also no way to get incommensurate or even minimally complex magnetic solutions: aka is not implemented

\*no temperature dependence of the solution...

Wrong wave function (HF or BS) can give acceptable total energy, but other properties may come out pretty poorly. One of the most important features is the gap opening when, say, an AF (Néel) state forms.



...thus a material must turn metallic *above* the Néel temperature..., it *never* happens... antiferromagnetic insulators remain insulators above the Néel temperature... ... it *is* the case for the metal – superconductor

transitions; SC *is* a gapped state and the gap closes above the transition temperature...

One may ask: are they really necessary these RVB states? Well... First one easily recognizes a potential of resonating structures in such well known things:



here, due to bipartite character of the lattices antiferromagnetic or other simple ordering is also possible ... but not always ...

### ... in the frustrated i.e. non-bipartite lattices simple ordering is *not* possible:

... one can try something more fancy:





spiral order, but in this case the energy gain is smaller than for a "Néel" state and RVB may become a real option...

... thus various combinations of various products of HL functions may enter into play and yield states of spin*liquid* (another name for *RVB*) type...







## ... only O 30 years ago Anderson suggested that RVB is a state of high- $T_c$ cuprate superconductors...

#### P. W. Anderson, Science 235, 1196 (1987)

The Resonating Valence Bond State in La<sub>2</sub>CuO<sub>4</sub> and Superconductivity

#### P. W. ANDERSON

The oxide superconductors, particularly those recently discovered that are based on  $La_2CuO_6$ , have a set of peculiarities that suggest a common, unique mechanism: they tend in every case to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. This insulating phase is proposed to be the long-sought "resonating-valence-bond" state or "quantum spin liquid" hypothesized in 1973. This insulating magnetic phase is favored by low spin, low dimensionality, and magnetic frustration. The preexisting magnetic singlet pairs of the insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly. The mechanism for superconductivity is hence predominantly electronic and magnetic, although weak phonon interactions may favor the state. Many unusual properties are predicted, especially of the insulating state.

Cuprate superconductors and the Hubbard Model . PW Anderson 1987



 $-\sum_{i=1,j<,\sigma}(t_{ij}+\mu\delta_{ij})(c_{i\sigma}^{\dagger}c_{j\sigma}+c_{j\sigma}^{\dagger}c_{i\sigma})+U\sum_{i}n_{i\uparrow}n_{i\downarrow}$ 

... thus, it is worth trying...
... to try one needs an object...

### with this in the toolbox we address CuNCN: simple structure...

### ... but peculiar physics

Paramagnetic... with two *T*-regimes, opens a gap...

... but no magnetic order...



### Heisenberg model... ...with RVB treatment



### Three RVB phases:

#### $C,B \neq 0; A=0$

 $A,B,C \neq 0$ 

 $A,C \neq 0; B=0$ 







### ...sequence of RVB phase transitions

Q1D-RVB	$T_c$	2D-RVB transient	coexist with	2D-RVB ground state
$B, C \neq 0; A = 0$	$\rightarrow$	$A, C \neq 0; B = 0$	$\leftrightarrow$	$A, B, C \neq 0$
$\chi = const$	100 K	$\chi \propto exp(-A/T)$	Δε≈30 K	$\chi \propto exp(-A/T)$

### .. structure manifestations of RVB phase transitions



### Experimentum crucis: heat capacity; measured minus lattice...



#### Atomic displacement parameters



 $\sum M_{\nu} \sum u_{i}(\nu) = \frac{\hbar}{4\pi} \int_{0}^{\infty} \frac{g(\nu)}{\nu} d\nu$ 

Sum rule:

experimental value on the left (graph): 7.6 Da·Å<sup>2</sup>; theoretical value on the right: 3.6 Da·Å<sup>2</sup> (VASP/PHONOPY).



#### Flexural mode:



0.1

0.0

0.3

0.0







60

T(K)

20

40

80

100

120

140

### Heat capacity with flexural mode



Shows features at two temperatures where the structural/magnetic manifestations had been detected: *ca*. 100 and *ca*. 20 – 30 K.

## How did you calculate this? What program you use?



What is thus the message? Life and physics are much more diverse and interesting than whatever program... and this brings...

### perspectives... ⊕⊕: 1D Hubbard (U<o)

#### U=-t; 10000 sites SC order parameter(T)





## OD Hubbard model

Energy optimization on superstructure wave vector  $Q \sim (\pi, \pi) + \delta Q(\pi, \pi)$ 





### Herbertsmithite – highly frustrated QSL



**Herbertsmithite** is a <u>mineral</u> with chemical structure  $ZnCu_3(OH)_6Cl_2$ . It is named after the mineralogist <u>Herbert Smith</u> (1872–1953) and was first found in 1972.

### Herbertsmithite $\rightarrow$ Kagome lattice of Cu spins



Frustrated Quantum Spin Liquid No long-range correlations for spins





### **Θ**Φ: Herbertsmithite – highly frustrated QSL



-2

0

ω

2

4

-4



### $\Theta\Phi$ : Summary

currently solvable by $\Theta \Phi$ :	solvable by $\Theta \Phi$ : in near future
Q-optimization of SDW states	Q-optimization in QSL and SC
Separate QSL, SDW and SC states	Arbitrary mix of QSL, SDW and SC
Small multi-orbital problems	Large multi-orbital
Simple $\rho$ symmetry	More involved $\rho$ symmetries
Basic thermodynamics	More thermodynamics and corr. Functions

### CONCLUSIONS

\*It is possible to construct *variational and topological* QM method for "organic" compounds (SLG is an option);

- \* within such a method structure formula (topological/iconic) directly corresponds to a wave function, different isomers refer to different possible wave functions;
- \*Either MO(CO)-LCAO or VB (one of the "lost tribes") do not exhaust all the possibilities. *Resonating* valence bonds – one of possible extensions (another lost tribe).

### \* Is that all? – No! – but some other time...

### Publications on the topic



- \* Monograph: Hybrid Methods of Molecular Modeling, Springer, 2008
- \* Papers: <u>http://www.qcc.ru/tch</u>
- https://www.researchgate.net/profile/And rei\_Tchougreeff/contributions
- Access to programs through the NetLaboratory system http://www.qcc.ru/netlab

# Thank you for your attention!