Adventures of Bond[1] In Wonderland

A.L. Tchougréeff

Chairman's remarks at the morning session of Workshop on *ab initio* Valence Bond theory on Friday, 20-th July 2012 (after the banquet).

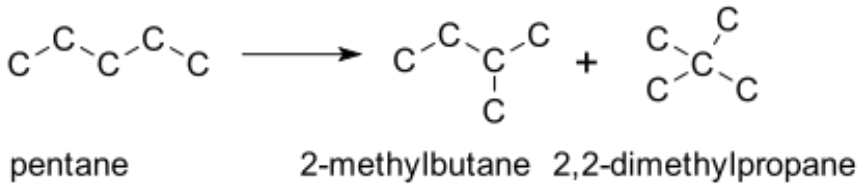
[1] Valence, of course, what did you think?

Frankland: 1852 (160 years, not that much)

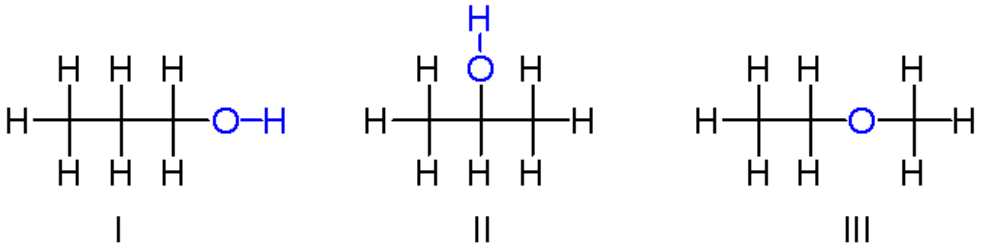
- Valence. Just a first name, not Bond (the last name) yet… In fact not even that…

Boutleroff: 1861 - 1864

What Boutleroff did? Coordinatization of the space of molecules by graphs…

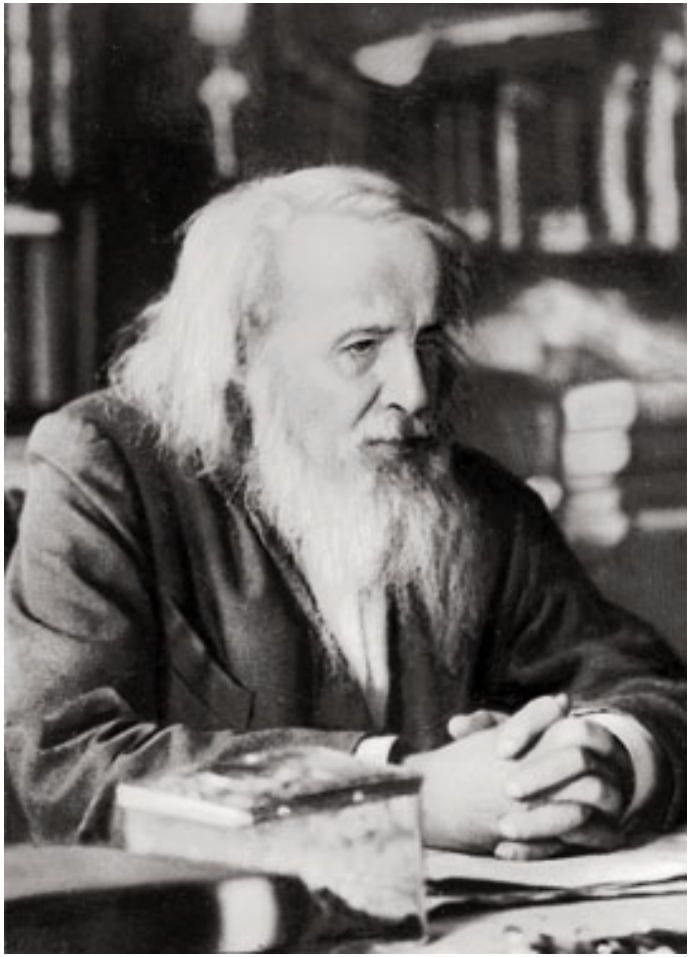


pentane 2-methylbutane 2,2-dimethylpropane



I II III

- «Assuming that to each chemical atom apartet (?) only a definite and restricted (limited ?) amount of chemical force (affinity), 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…»
- «… chemical nature of a composite particle is stipulated by the nature of its elementary component parts, their quantity and chemical structure»

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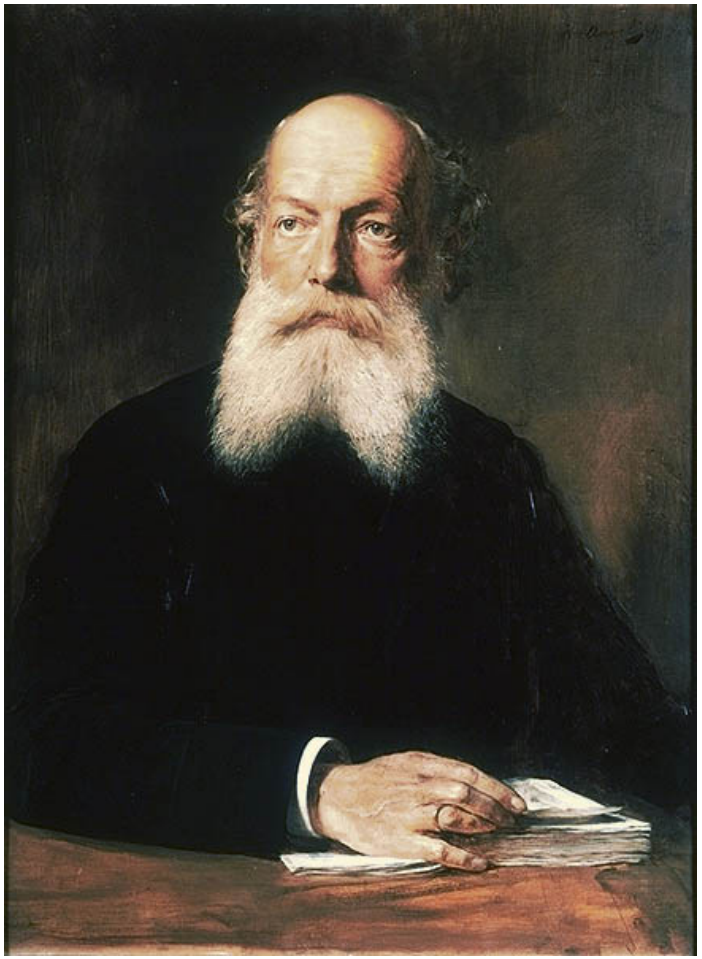
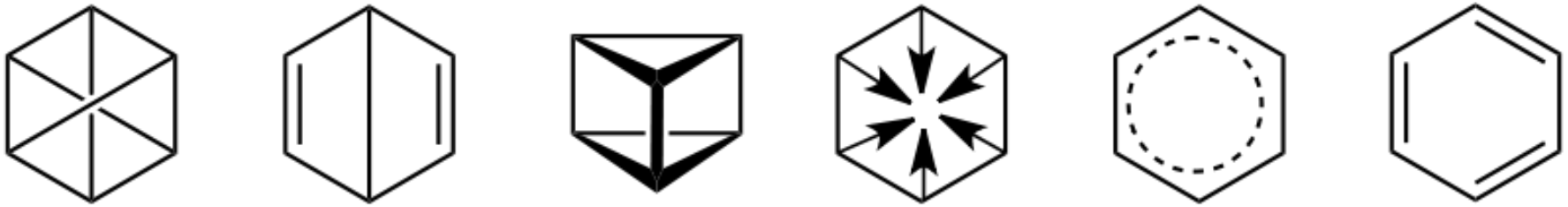
Kekulé: 1865

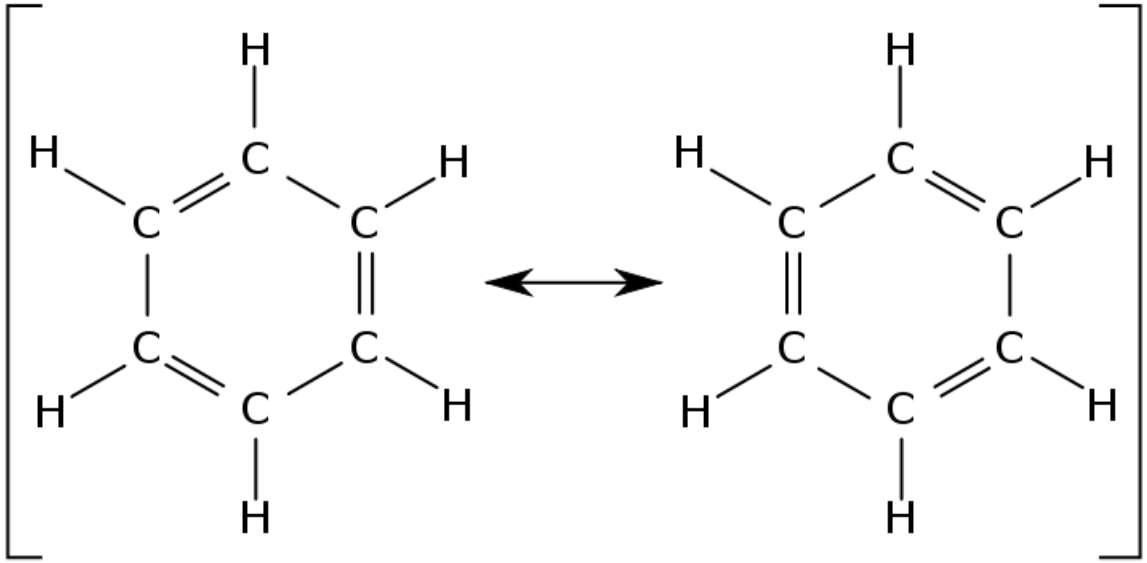




Historic benzene formulae

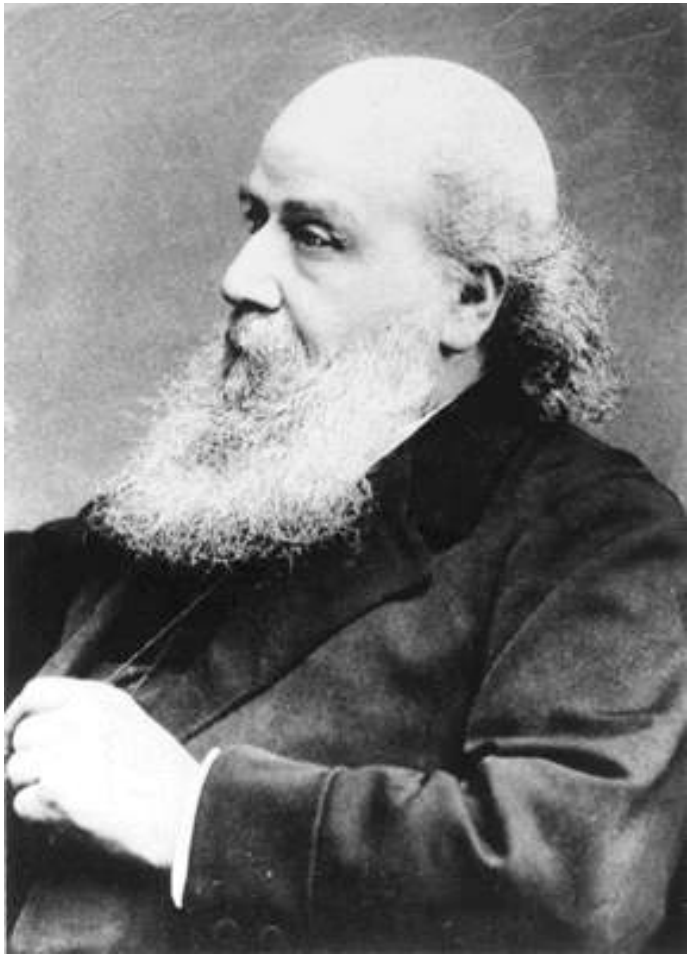
Respectively, by Claus (1867), Dewar (1867), Ladenburg (1869), Armstrong (1887), Thiele (1899) and Kekulé (1865). Dewar benzene and prismane are different chemicals that have Dewar's and Ladenburg's structures. Thiele and Kekulé's structures are used today.

Benzene oscillates between two Kekulé structures…



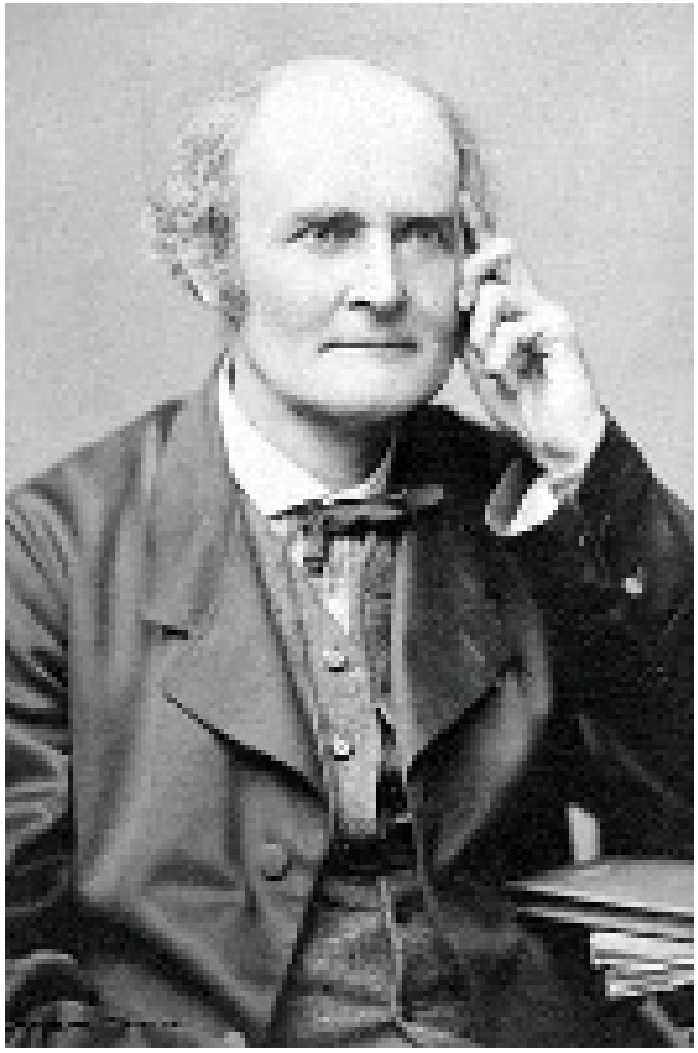
Already Kekulé himself had been convinced through his discussions with Ladenburg that a model with three double and three single bonds is not good. So he finally said that it *oscillates* between these two structures… whatever it means…

Sylvester: 1878



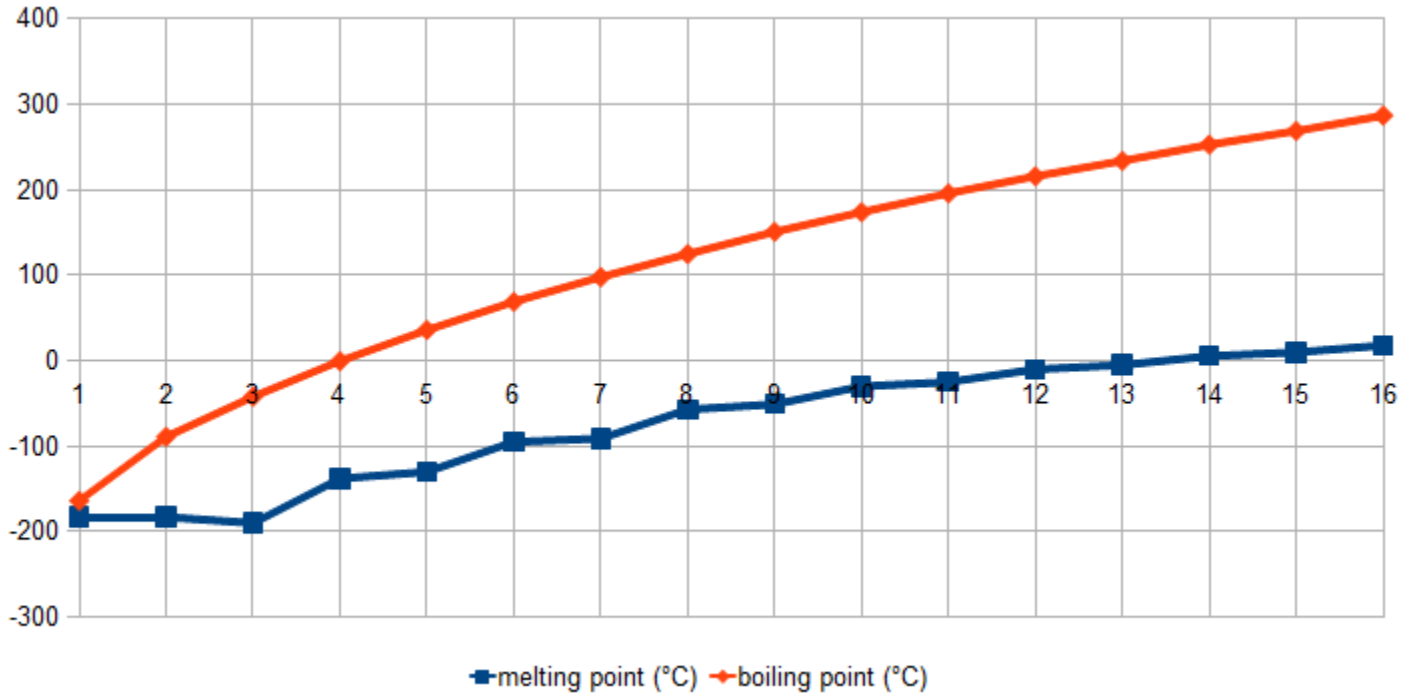
- Introduced valence bond wave function without knowing what is electron, what is wavefunction, what is whatsoever…
- Published about 1000 papers which complete 4 volumes. Among them
- American Journal of Mathematics, Vol. 1, No. 1 (1878), pp. 64-104…

- “The factors of any algebraical form may be regarded as in some sense the analogues of the rays of atomicity in the equivalent chemical atom these rays being what Dr. Frankland, according to his nomenclature, would have to designate as free bonds; such rays between two consecutive atoms in a molecule are conceived as blending in some manner so as to represent some unknown kind of special relation existing between them; they may then with propriety be called bonds or lines of connexion”. [J.J. Sylvester. On an Application of the New Atomic Theory to the Graphical Representation of the Invariants and Covariants of Binary Quantics, with Three Appendices.]



C. Schorlemmer

What Schorlemmer did?
Melting and boiling points of alkanes.



What did Caley?

Alexejeff & Gordan: 1900

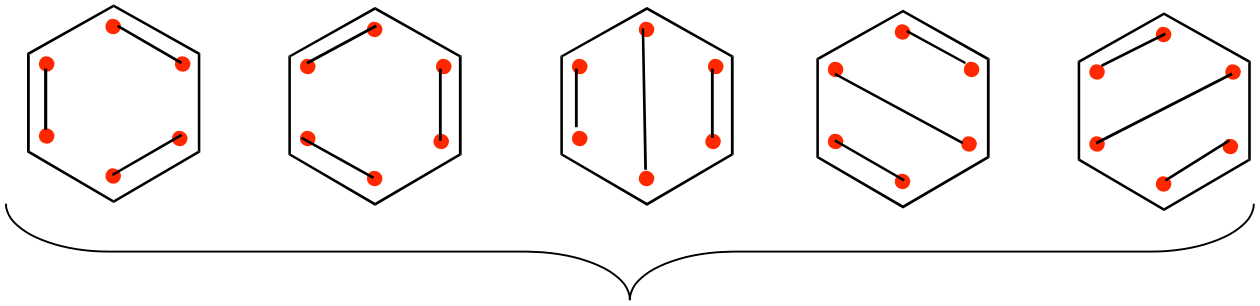
Paul Albert Gordan: the king of invariant theory.

Wissarion Grigorjewitsch Alexejeff

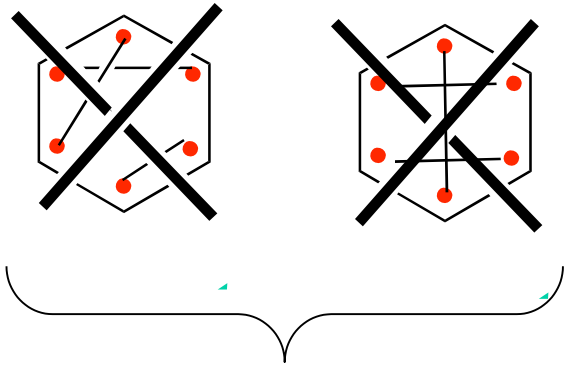
London, Heitler, Weyl, Rumer




What did Rumer do?

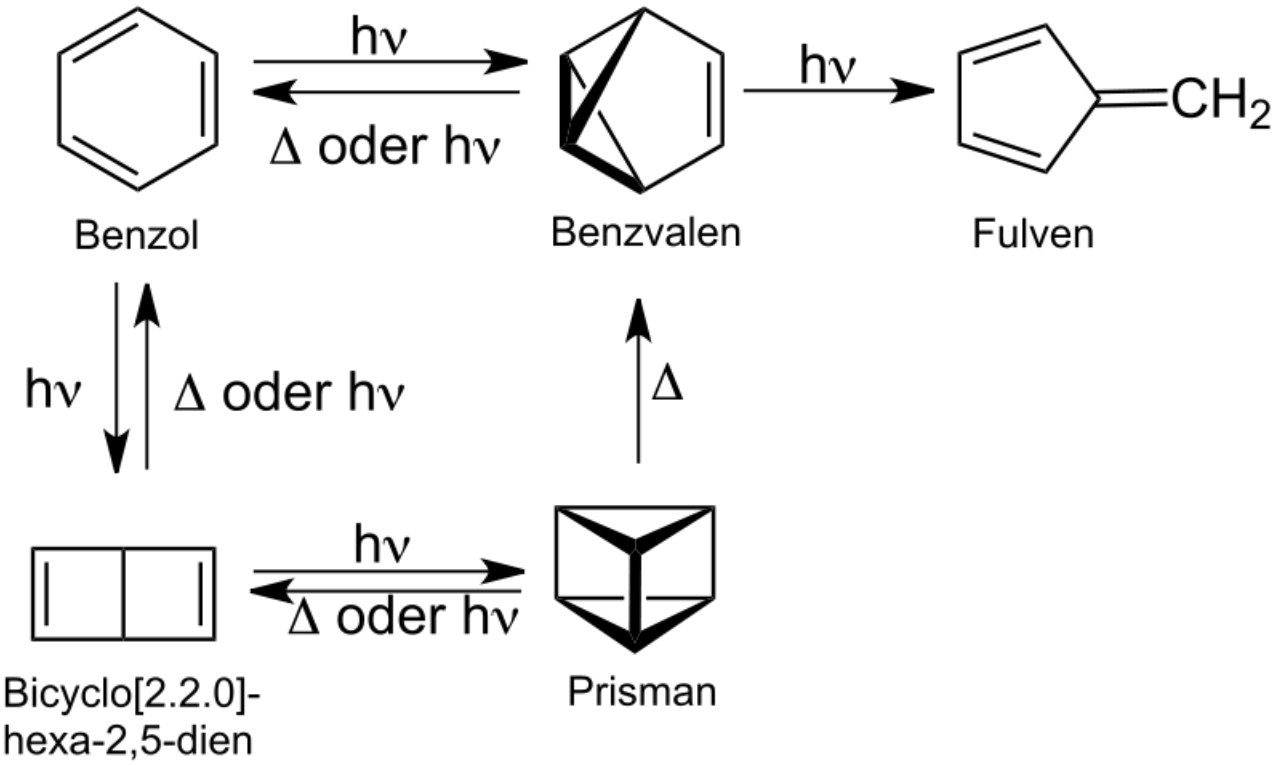


Good

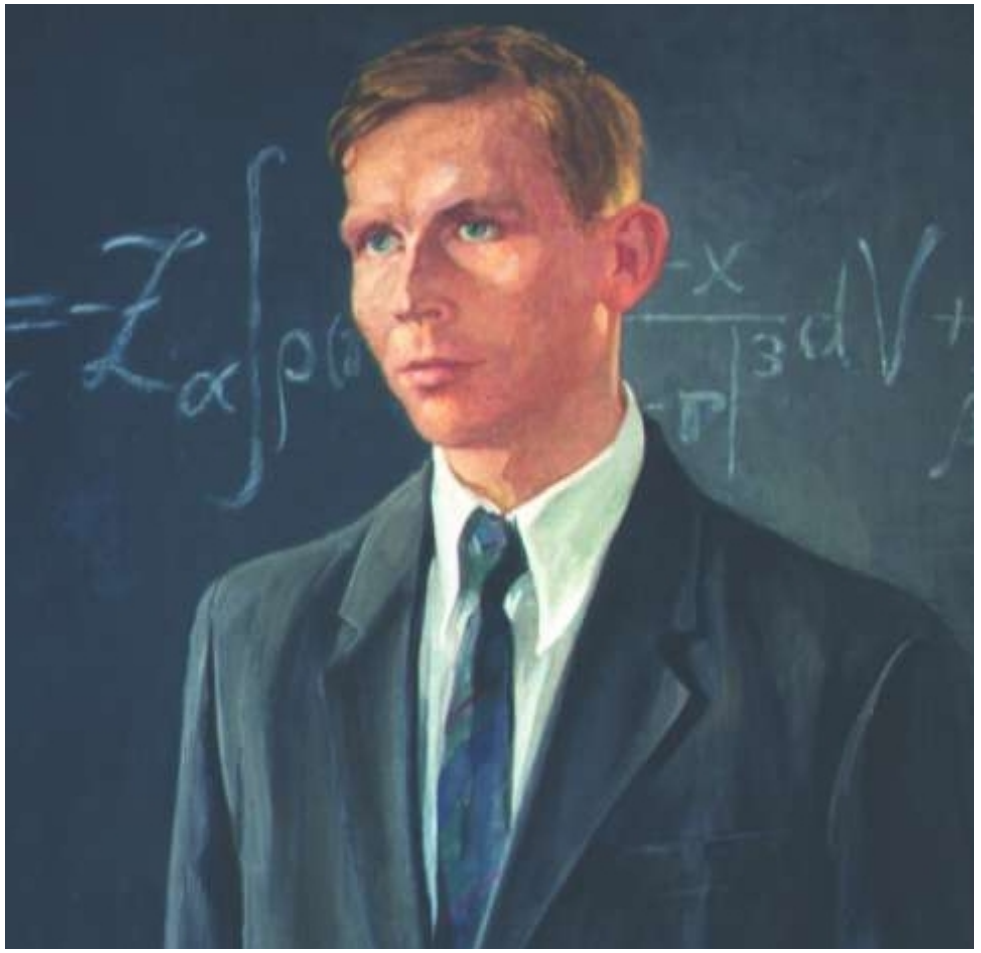


Bad

BUT!...


hν
Δ oder hν
hν
CH2
Benzol
Benzvalen
Fulven
hν
Δ oder hν
Δ
hν
Δ oder hν
Bicyclo[2.2.0]-
hexa-2,5-dien
Prisman

Fock & Hellmann




ИППИ

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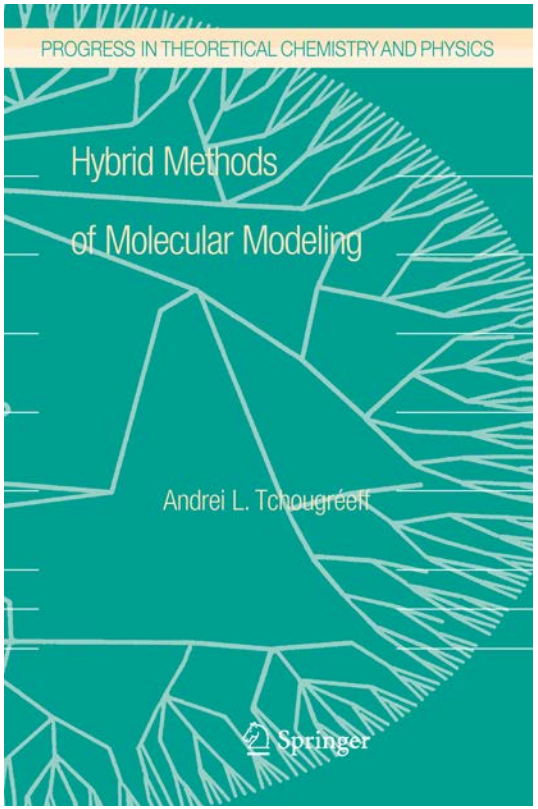
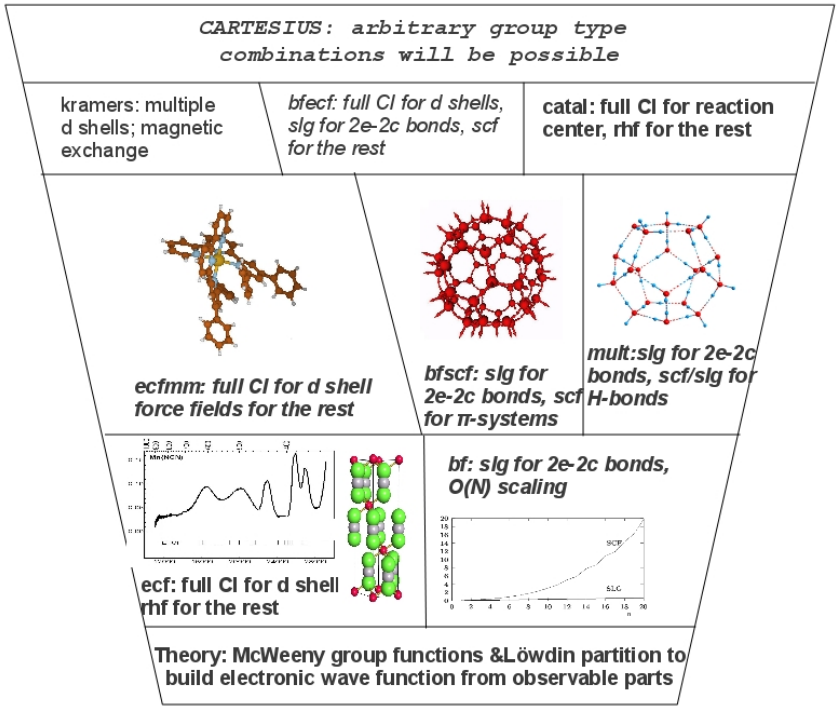


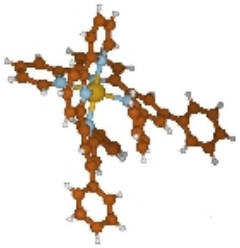


CARTESIUS: arbitrary group type combinations will be possible

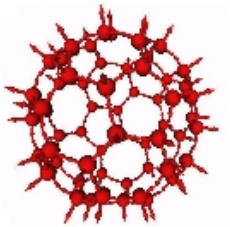
kramers: multiple d shells; magnetic exchange

bfecf: full CI for d shells, slg for 2e-2c bonds, scf for the rest

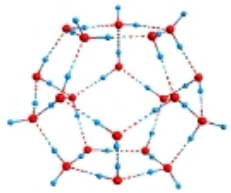
catal: full CI for reaction center, rhf for the rest



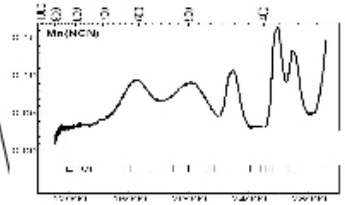
ecfmm: full CI for d shell force fields for the rest

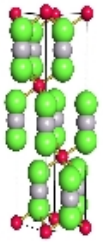


bfscf: slg for 2e-2c bonds, scf for π-systems



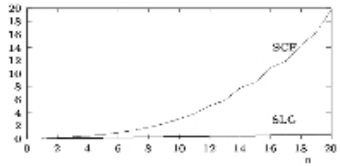
mult:slg for 2e-2c bonds, scf/slg for H-bonds





ecf: full CI for d shell rhf for the rest

bf: slg for 2e-2c bonds, O(N) scaling



Theory: McWeeny group functions &Löwdin partition to build electronic wave function from observable parts

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