Synthetic Quantum Chemistry

I
Rüdenberg's Integral Approximations and their Weighting Extensions.

II
Orbital Theories of Hartree-Fock-Rüdenberg Type for Large Molecules and Crystals.

III
Electrons, Chemions and the Aufbau Principle of Molecular Quantum Theory.

Chemials and Chemionic HARTREE Configurations
as Elements of a Modular Quantum Chemical Picture.

IV
Chemistry, Quantum Mechanics and Reductionism.

Synthetic Perspectives for Theoretical Chemistry
in the Spirit of HANS PRIMAS' Ideas.

Synthesizing a complex molecule is an art which knows to develop a strategy for finding appropriate reaction pathways via a couple of stable intermediate compounds. Not so the art of constructing electronic wave functions: Non-empirical quantum theories, viz, usually make no efforts to start from chemical intermediates. They rather consider each molecular HAMILTONian as an essential physical operator to be recomposed again and again by adding all elementary energy contributions (like the electrostatic COULOMB interactions between electrons) from the very beginning ("*ab initio*"). Comparable synthetic strategies for first-principles' quantum chemistry are not in common use.

The difficulties in establishing a quantum chemical "*Baukastenprinzip*" essentially stem from the holistic nature of quantum physics itself (PRIMAS [1]). Certainly: Localization criteria [2], population analyses [3], and BADER's appealing "*Atoms in Molecules*" concepts [4] enable us analytically to reconstruct the atomistic stick-and-ball picture of chemical common sense from readily calculated *ab-initio* results. There are only few attempts, however, to realize a synthetic prescription. At least one approach of building-up a quantum-chemical matrix representation of the molecular HAMILTONian from precomputed elements indeed exists [5]. But neither this technique nor other theories which focus on a more chemical view [6] seem to be frequently applied today.

Nevertheless there is some evidence, that a quantum chemical *Aufbau* principle based on atomic or other compact entities may prove to be valid:

- Already in 1931, HÜCKEL suggested an atomic connectivity matrix as being essential and sufficient for the explanation of aromaticity [7].
- Starting from an earlier recipe of WOLFSBERG and HELMHOLZ [8] for the estimation of HAMILTON matrix elements using atomic ionization potentials as empirical parameters, HOFFMANN's "*Extended Hückel Theory*" (EHT) [9] lead to the formulation of the famous "*Woodward-Hoffmann rules*" [10] concerning a special class of stereoselective recombination reactions.
- The renaissance of density functional techniques (based on theorems due to LÖWDIN, HOHENBERG and KOHN [11]) teaches us, that condensed quantities may become favourable compared to standard orbital descriptions.

Note that there are also other genuine atomistic concepts of general acceptance like the

- BORN-OPPENHEIMER approximation [12]

and the

- "*Linear Combination of Atomic Orbitals*" (LCAO) [13],

which already introduce a great deal of chemical understanding into the original quantum physical framework.

Suggesting a dominantly local nature of necessary relativistic and correlation corrections we ask: What kind of approximations or even violations of quantum physical laws can be justified in order to establish a synthetic quantum chemical *Aufbau* principle which allows to start from localized and predetermined modules ?

This question serves as a common denominator for the four sections of the present work. Though an answer will only be risked in the third part, the HARTREE-FOCK-RÜDENBERG picture (HFR) of the second paragraph can already be looked at as an instructive intermezzo: it shows that HOFFMANN's semi-empirical EHT is compatible with the non-empirical HARTREE-FOCK method in ROOTHAAN's form [14]. Disregarding its technical advantages, HFR thus explains why EHT turned out to be qualitatively successful. Such insights into the first-principles' fundaments of "*Extended Hückel Theory*" could only be gained by reinspection and extension of RÜDENBERG'S early ideas. The preliminary studies of the first chapter, which is devoted to this topic, are of general importance for both subsequent parts.

The "*chemion theory*" outlined in the third section has the face to postulate a limited validity of the PAULI principle for large molecules. Moreover, single electrons are no longer considered as being the proper actors of macro-molecular chemistry. Consequently, molecular orbitals are substituted by molecular "*chemials*", and the tremendous number of SLATER determinants introduced in electronic structure theories reduce to a moderate and size-consistent set of "*chemionic Hartree configurations*".

The precision to be expectable from such a treatment cannot reach any reductionistic (i.e. electronic) quantum chemical standard, of course. The strength of the chemionic view, however, rather relies on its interpretability in terms of classical concepts like VAN'T HOFFs atomistic picture [15].

Introducing new quasi-particles like our chemions, one acts as a "*fabricator mundi*". Doing so was mainly encouraged through the unique book "*Chemistry, Quantum Mechanics and Reductionism*" of HANS PRIMAS [16]. His profound analysis of present-day theoretical chemistry has always been a guide for our intentions and ideas. While stressing the synthetic perspectives of chemion theory, in section IV we finally discuss its scientific status using PRIMASian terminology.

References and notes

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