CARTESIUS FORT - OBJECT FORTRAN Library for Chemistry and Materials Science

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Abstract. Modeling of structure and properties of molecules and materials (crystals/solids) on the basis of their electronic structure is one of the most important consumers of computer resources (processor time, memory and storage). The known attempts to improve its efficiency reduce to massive parallelization. This approach ignores enormous diversity of types of structures and behaviors of molecules and materials. Moreover, this diversity is by no means reflected in the paradigm currently dominating the field of molecular/material modeling.

Much more efficient is, of course, a thorough analysis of the physical conditions occurring in different molecules/materials. On this way we could successfully build a series of efficient methods targeted upon specific classes of molecules/materials: inorganic ones with open *d*-shells and organic ones featuring local two-center bonds and developed conjugated π-systems (generalized chromophores).

The experience gained formulates as a new concept of semi-empirism: that is selecting the electronic wave function of a system under study as a product of the wave functions of the chromophores present in the system. This called for a new development: of a library of objects representing different types of chromophores to be freely combinable to represent an arbitrary molecule/material so that its respective parts (chromophores) are modeled by the most efficient method suitable for the specific type of the chromophore and taking into account the interactions between them. Apparently, the deep segmentation of the system achieved within the new concept of semi-empirism allows for the efficient parallelization and more efficient usage of the HPC software.

Keywords: New concept of semi-empirism · Polymorphic trees · Generalized chromophores · Cartesius fort library

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1 Motivation

1.1 Quantum Modeling Issues

Molecular or materials' modeling relying upon analysis of their electronic structure (quantum chemistry) is one of the largest consumers of the computer resources in terms of processor time, memory and storage. The reason for this is twofold: realistic models include large numbers of atoms to represent namely that system whose properties are modeled and it may be fairly large - hundreds to tens thousands of atoms - when it comes to processes in living matter or to technological (*e.g.* catalytic) processes. In the realm of materials' modeling the "size" of the realistic model is the number of atoms in the unit cell of the modeled crystal. In case of popular modeling objects like zeolites (Fig. 1 left) or metal-organic frameworks (MOF's - Fig. 1 right) it may reach hundreds or even thousands. These amounts determine the costs of modeling which for a system with open d-shells may scale as $O(N^7)$ where N is the number of atoms included in the model for standard modeling methods based on the wave functions. An alternative frequently portrayed as a "method of choice" for the materials (crystals/solid state) modeling - the DFT based methods - frequently face the convergence problems. In a recent study Ref. [1] more than 2600 published MOF structures had been processed by a DFT+D3 program the convergence has been reached in slightly more than in one third (!) of cases.

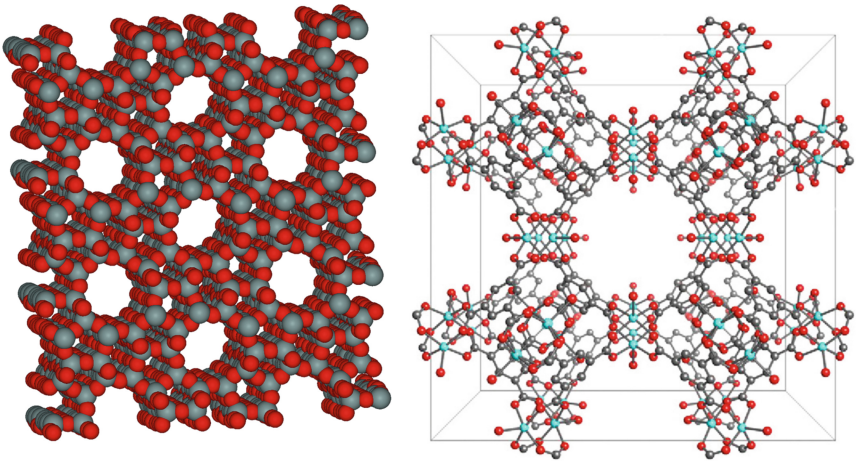

Fig. 1. Characteristic objects of materials modeling. Left: zeolite (ZSM-5); right: iron(II) containing MOF (Fe-BTC).

The DFT-based methods [2–4] (similar to one used in Ref. [1]) portray the electronic structure of, say, NiO as formed by Bloch states delocalized over the entire crystal and ascribe the observed anti-ferromagnetic ground state of this

and other similar - very simple - crystals to opening of the gap in their one-electron spectrum [5]. This picture is *physically incorrect* (!): had it been true, NiO and other similar materials would have to become *metals* above respective Néel temperatures which is definitely not the case: they remain insulating and the values of the *local* momenta in the paramagnetic phase are almost the same as the saturation momenta in the anti-ferromagnetic one. The same was shown for "organic" analogs of transition metal oxides: simplest possible MOFs: transition metal carbodiimides of the general formula MNCN, M = Fe, Co, Ni [6,7]. Another fresh study [8] addressed a couple of rather simplistic Fe(II) complexes with use of a series of DFT functionals. It turned out that these functionals produce the energy differences between the ground high-spin and first excited low-spin states in the range from minus to plus 30 kcal/mol (more than 1 eV); *neither* of them was capable to give the correct *experimentally known* energy gap. The DMRG-CASPT2 method used in Ref. [8] for control does not help: in either case the ground state was incorrect.

The intrinsic complexity of the modeling problems either in molecular or in the materials' (solid state) contexts is aggravated by the paradigm dominating the field, which can be characterized as *naïve monism*. It represents a strong belief that the entire system must be modeled at the same, possibly most advanced level of theory. Practically it leads to the prohibitive computational costs mentioned above, but even these cost are spent in vain: the results are wrong (see [8] and references therein). It would be unfair to say that nothing is undertaken in the literature to avoid this. Attempts to take into account nonuniformity of molecular systems are known as hybrid quantum mechanics/molecular mechanics (force field) - QM/MM - methods which according to Ref. [9] "can be applied whenever one needs to model a localized electronic event in an active site (typically of the order of 100 atoms) that is influenced by an interacting larger environment". Obviously, 100 atoms is too much for a systematic application of $O(N^7)$ scaling methods.

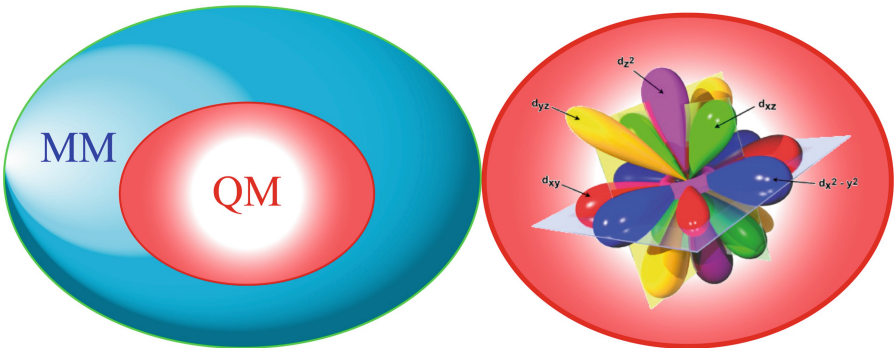

Fig. 2. Pictorial representation of the separation methods in the standard (hybrid) QM/MM methods (left) and in effective crystal field method (right)

The patterns of separation practiced in the standard QM/MM methods are, however, not fully consistent with quantum mechanics. The standard way is to set the quantum/classical boundary in the real space Fig. 2 (left) ignoring that bonds are broken by such boundary. A considerable list of *ad hoc* recipes to be used to handle the violation of quantum mechanics is given in Ref. [9] (see also references there), their critical analysis is given in Refs. [10–12].

1.2 Cheminformatics Issues

Representing chemistry objects in the computer codes is a cheminformatics problem [13]. It is usually addressed without explicit reference to electronic structure of molecules and materials. This approach runs into problems (inherited by the systems of computer coding of molecules and compounds [14,15]) which can be understood if one analyses the situation with the chemical nomenclature in general. While doing so one immediately recognizes that the situation drastically differs in "organic" and "inorganic" chemistry (the latter must be understood in a general sense: including coordination and organometallic chemistry). The "inorganic" realm (incidentally, including MOFs) is extremely diverse whereas "organic" realm is much more uniform, contains much smaller repertory of atoms. The "inorganic" realm contains kind of simplistic subset (basically taught in high school) where the compound can be fully characterized by its composition: KCl, H_2O etc. Switching to the "organic" realm changes the situation completely: even simple composition C_2H_6O does not characterize the thing completely: two different substances represented in Fig. 3 correspond to it. The very simple question arises: what in reality represent Fig. 3 (the structure formulae of organic chemistry)? What are these sticks? Everyone would say "what a stupid guy is him!" - these are bonds! But what are bonds? Here reigns a complete confusion: "The concept of bond appeared little by little in the mind of chemists from empirical observations. From the wavemechanical viewpoint it is not an observable."[16] - not bad, isn't it? So what do then they draw these stupid chemists? non-observable? The chemists are numerous and strike back: they form an International body IUPAC which gives definitions from the position of authority. They are subject to complete change *c*a. every 10 years [17,18] without notice and contain vicious circles.

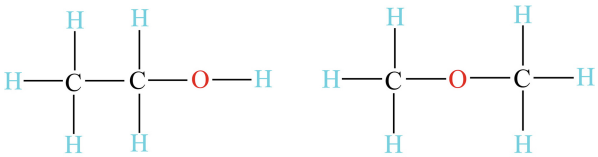

Fig. 3. Classical structure formulae of two isomers of archetypical C_2H_6O composition.

Amazingly the solution was known well before all this confusion had any chance to appear. Yet in 1900 Gordan (that one which is Clebsch-Gordan) and Alexejeff published a remarkable paper [19] entitled "Übereinstimmung der Formeln der Chemie und der Invariantentheorie" that is "coincidence of the formulae of Chemistry and Invariants Theory" where they could show that the pictures drawn by organic chemists are in one-to-one correspondence with functions of complex 2D vectors belonging to a special class called *invariants* (in contemporary terminology spin-invariant or spin-singlet). For more detailed discussion see Ref. [20]. Apparently it is nothing, but an abridged notation to the valence bond (VB) wave functions [21] depicted in Figs. 4 and 5.

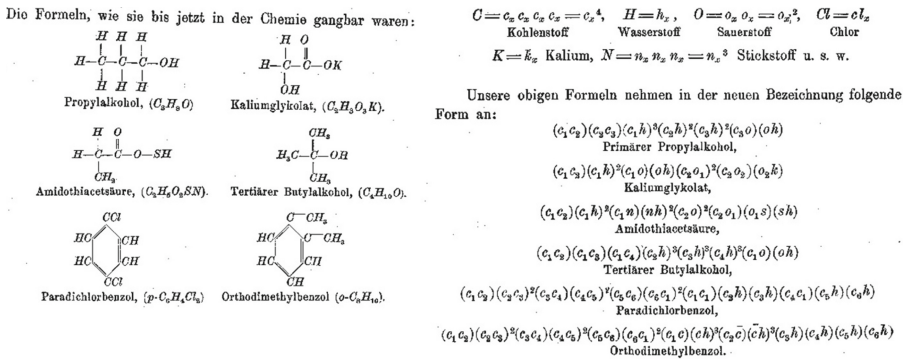

Fig. 4. First in the history pictorial representation of the isomorphism between structure formulae of organic chemistry and invariants of complex 2D-vectors.

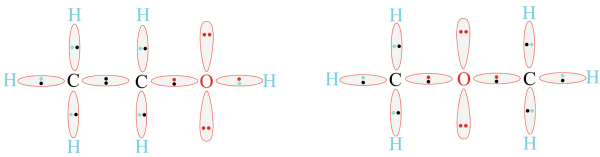

Fig. 5. Pictorial representation of the valence bond wave functions corresponding to classical structure formulae of two isomers of C_2H_6O.

The isomorphism between 'classic organic chemistry' and invariants means that everything which can be drawn according to the "rules of organic chemistry" is an invariant of the prescribed form and nothing else can be drawn (without breaking these rules). This predetermines either the enormous strength of the "normal" language of organic chemistry, but also its deficiencies. The most modern cheminformatics descendant of the 'classic organic chemistry' - InChI, "is able to handle almost 99% of the chemicals which scientists are concerned with every day" [22] at the same very time excludes entire areas of chemistry: "Organometallics, inorganics and other classes of compounds still present a significant challenge" [15]. Thus, the ambitious "eventual goal to extend InChI to

cover all of chemistry", is effectively postponed. The reason is that "No widely accepted means of representing organometallic substances exists" [23], but why it is so? From the point of view of quantum theory of molecular electronic structure the exceptions are remarkable and characteristic: (i) Not all molecules have electronic structure of the form of invariants which GA meant - those which are formed of local electronic spins: there is benzene and other similar (aromatic, but not only) compounds, featuring "delocalized" 2D vectors (spins) of which the required invariants are formed. Of course, aromatic and other similar molecules are too ubiquitous, so that numerous workarounds have been developed to represent them. Nevertheless, the very classical model of bonding is too restrictive which when pushing it through like in InChI leads to information losses: "All bonds are simple links (connections). That is, they have no "double", "triple" or other attributes". (ii) Not all molecules are spin invariants: dioxygen is the most well known exception, but had it been only one exception a plausible way out would be found. However, not unique exception, rather entire areas of chemistry (pretty good portion of inorganic, the whole coordination and tentatively organometallic chemistry) formed by such exceptions - transition, rare earth, actinide compounds are not spin invariants since their ground states are not spin singlets.

The fact that some molecules (benzene the best known example) cannot be represented by a single invariant of the GA form, that is, are not covered by the 'classic organic chemistry' led to an alternative idea [24] eventually overcoming its deficiencies. It, first of all, suggests to distinguish σ- and π-electrons, allows multicenter bonds (inclusive what is called 'coordination' ones), eventually allowing, to describe, say, ferrocene more or less uniquely, as a system composed of 10 σ-C-H- and 10 σ-C-C-bonds supplied by a multicenter (in fact 11 centers) 'bond' formed by 18 electrons. A defect which probably prevented from a wider usage of this fairly perspective approach (it, meanwhile, is not employed in InChI) was its heavy reliance upon the description of the molecular electronic structure coming from some calculation which is thus dependent on applied computational method. As in case of 'classical' bonds, the solution has been proposed long ago. The physically substantiated indexing of molecules must be based on observable elements of their electronic structure. Such elements has been originally proposed in Ref. [25] where the name 'chromophore': a part of molecule giving color to it, has been coined. These are apparently observable (even visually). In organic realm the chromophores are usually rather large conjugated π-systems. The idea of observability of components of molecular electronic structure has been generalized to bonds [26] and can be further extended [10,20].

2 Proposed Solutions

Не в совокупности ищи единства, но более – в единообразии разделения. — К. Прутков.[1]

We see that the problems encountered either in modeling or in simply uniquely naming extremely diverse chemical species (molecules or materials) stem from attempt to squeeze this diversity in a monistic picture. In cases when the nonuniformity of physical conditions is recognized (QM/MM) the separation is described as one into "interesting" and "uninteresting" parts to be treated, respectively, at a "higher" (QM) and "lower" (MM) level methods and performs in the real space. Among other issues it leads to the necessity to make the QM part 'as large as possible'.

Any attempt of segmentation of the physical object on the basis of "interest/uninterest" is of course a solipsistic nonsense. The true basis of separation can be only the real localization of the lowest energy excitations in that or another part of the system. In variance with wide spread (mis)concept (setting boundaries in the real space) the true separation is to be performed in the Hilbert space, as it was clear yet to the inventor of such a separation [27] and reiterated in [20], that is the parts of the system are orthogonal subspaces of the orbital space of the molecule.

2.1 Preliminary Studies

In the realm of the molecules and materials with open d-shells we face a very unpleasant situation: the "method of choice" produces a wrong physical description of simplest representatives of the target class of compounds: the compounds of transition metals with some "organogenic" atoms. One can foresee that in other areas of molecular and materials' modeling it is not much better. What could be the way out? Our proposition is rather old-fashioned: instead of applying machine learning to the heaps of wrong "big data" obtained by inappropriate methods, to try to figure out the physical reasons of the failures and to take care of them. An alternative to mindless computation is, of course, a detailed analysis of physical conditions in different parts of the molecular system.

Transition Metal Complexes. A thorough analysis shows (and it can be expected in the systems of electrons subject to the *singular* - Coulomb potentials) that, in fact, the physical conditions in different parts of the objects which one might be willing to model are quite different. Yet in Ref. [28] we noticed that the ratio of the Coulomb interaction between electrons in the d-shells to the resonance interaction of these orbitals with other orbitals is much larger than say in π-system of benzene. Indeed, in the $[NiF_6]^{4-}$ anion the ratios of the one-center Coulomb repulsion parameters to the resonance integrals between Ni orbitals and F $2p$-orbitals are about 50 for $3d$-orbitals, about 1.5 for $4s$-orbitals, and about unity for $4p$-orbitals of the Ni atom [28] (analogously for other complexes).

[1] Not in totality seek for unity, rather in uniformity of separation—K. Prutkov.

Similar ratio for π-orbitals in benzene is about four. Harrison notes the similar situation in magnetic insulators and crystals with paramagnetic impurities [29]. In this case, when the Coulomb interaction turn out to be more significant than the interatomic interactions dominating the band structure calculations (the Coulomb-to-resonance ratio $\gg 1$), electrons in the crystal are to be described with use of local rather than delocalized Bloch states. The spectrum of the crystal (for example NiO) coincides with the band spectrum of the simple ionic crystal CaO complemented by the spectrum of d-shells split by the crystal field. This picture drastically differs from the ideas underlying the standard modeling methods [2–4].

In the case of transition metal complexes with open d-shells and the corresponding solids the clue is provided by the good old crystal field theory [30] proudly celebrating its 90-th anniversary this year. It produces the correct phenomenological description of the ground states and spectra by considering *only* the d-shells with fixed numbers of electrons split by the external field of the relevant symmetry. By this the problem of describing problematic transition metal compounds separates into two simpler ones: (i) to calculate the effective field induced by the environment upon the d-shell and (ii) to calculate the many-electronic (multi-reference) states of this shell with the fixed number of electrons. This approach fairly follows the main Cartesian idea: "Diviser chacune des difficultés afin de mieux les examiner et les résoudre" [31] and turns out extremely efficient: dozens of complexes has been calculated (see Fig. 6); none of them has manifested an incorrect ground state spin and symmetry, even highly problematic Fe(II) spin-active complexes could be successfully reproduced [34,35], including the relative energies of the spin-isomers with an unprecedented precision. Our approach allowed us to *reduce* as much as possible the sizes of the parts of the system (electronic groups) requiring application of numerically demanding methods. *E.g.*, singling out d^n-shells represented in Fig. 2 (right) fits the way of classification of transition metal complexes accepted in the compendium of their electronic spectra [32] where they are considered as chromophores. It eventually provides the way around the complications of the classical model of chemical structure and the representation problems related to it. For example, Fe(II) complexes (Fig. 6) are completely described by the list of σ-bonds, π-systems, complemented by the d^6-chromophore and by a chromofore for which a name of *close ligand shell* has been coined in Ref. [33]. This representation is eventually unique.

2.2 Formal Description

The example of transition metal complexes was extremely instructive in many respects: most important, it allowed us to break with the dominant paradigm of ostensible universality of the "unique" methods and to switch to object-targeted methods - those whose very structure is stipulated by that of the molecules/materials under consideration.

Reflecting the diversity of chemical (electronic) structures missing in *monistic* representations of electronic structure either in molecular/material modeling

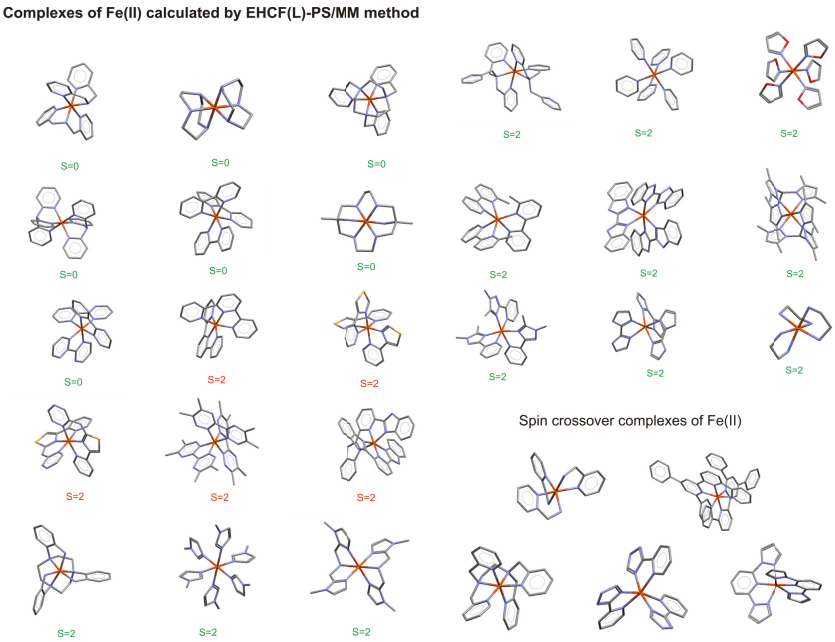

Fig. 6. A selection of Fe(II) compounds problematic for DFT and CASPT2 methods on the basis of effective crystal field theory. Green marks coincidence of the ground state spin with experiment, red - disagreement. For (experimentally) the spin-crossover complexes the respective (correct) ground state spins are reproduced for the respective geometries.

or in cheminformatics when achieved has a perspective to considerably improve the performance of both of them. The most abstract representation of the molecular (material) electronic structure through their observable parts (generalized chromophores) is given by the group function approximation:

$$\Psi_0 = \bigwedge_{m=1}^{M} \Psi_m \tag{1}$$

where $\wedge$ denotes the antisymmetrized product of the multipliers following it. The functions Ψ_m are the N_m-electron functions for respective chromophores built the carrier subspace L_m for the m-th chromophore. The carrier subspaces of the chromophores are orthogonal and formally express as follows:

$$\begin{gathered} L = \bigoplus_m L_m; \dim L_m \geq N_m \\ L_m \cap L_n = \{0\}, m \neq n; \end{gathered} \tag{2}$$

This alternatively expresses through projection operators:

$$\begin{gathered} \sum_m P_m = I; P_m P_n = \delta_{mn} P_m \\ L_m = \mathrm{im} P_m \end{gathered} \tag{3}$$

Releasing the condition Eq. (3) to

$$\begin{gathered} L = \bigoplus_m \mathrm{im} P_m; P_m P_n = P_m \\ (L_m = \mathrm{im} P_m) \subseteq (L_n = \mathrm{im} P_n); L_m \cap L_n = L_m \end{gathered} \tag{4}$$

reveals the tree structure of the carrier subspaces with the entire space L as a root and the carrier subspaces for the generalized chromophores as leaves.

Molecular/material modeling provides ample space for tree structures. Fairly analogous to the tree of the carrier subspaces the entire space of the atomic (nuclear) coordinates of the molecular model is the direct sum of the $\mathbb{R}^3$ spaces of the Cartesian coordinates:

$$D = \bigoplus_a \mathbb{R}^3_a \tag{5}$$

The entire coordinate space D represents the root of the corresponding tree (a runs over the entire set of atoms/nuclei). Introducing the tree structure by sequentially applying orthogonal projection and orthogonal transformation operators in the corresponding image subspaces allows one to define the collective geometry coordinates. This may/must be done consistently with the chemical structure which in its turn as well represents a tree structure formed by the groups (Gerhard's *radicals*) like methyl, phenyl, *etc.* The geometry variation/optimization is then possible in terms of such collective coordinates as the position of the center of mass of a *radical* and orientation of its inertia tensor principal axes relative to whatever other frame.

2.3 Implementation Details

With those ideas in mind we some time ago launched the development of a program library capable to cope with the problems described in previous Sections. It implements the results of the analysis of the structure of the hybrid methods of molecular/material modeling performed in Refs. [10,34–36]. Presence of several tree like structures calls for a generic tool for representing them. With use of trees the molecular models structure in a natural way: following their chemical segmentation, allowing for the construction of the models in terms of molecular fragments (Gerhard's radicals). Basically, neither of the "big" languages (JAVA, C++, FORTRAN) intrinsically supports trees. However, the demand for them was fairly clear already many years ago. This demand enters into contradiction with the way the "big" languages are designed (uniformity of the components of "collective" data types). Nevertheless, within the latest years the development of the FORTRAN compilers [37] has advanced that much so that the many features available in the "high-level" languages (*e.g.* Python) can be implemented. Thus, it seemed to us that the amount of investment into developing of the missing collective data types in FORTRAN is smaller as compared to that required to rewrite in a "modern high-level language" the whole supply of the specific code relevant to molecular/material modeling (also with the account of the availability of more general mathematical software in the "big" languages) and we undertook some

effort in this direction. Specifically, we developed a module POLYMORPHIC_TREE which allows an arbitrary content of the tree's node and provides basic functions of adding/deleting nodes/subtrees, addressing (getting and modifying) the node content by their identifier/name, traversing (recursively) the nodes/leaves, *etc.* This development eventually makes the features so far existent in the languages like Python available in FORTRAN making it "high-level" *per se*. This allowed us to profit from the available (previously developed) scientific FORTRAN code [38].

Analogously to *polymorphic trees* even simpler universally *polymorphic lists* and *pairs* had been implemented which eventually made available in FORTRAN another very useful abstract structure - dictionaries: lists of pairs (key, value[2]) both being pointers to universally polymorphic types (class(*)). Universally polymorphic lists/pairs allow to attach extensible lists of properties (attributes) to the nodes of a tree representing molecular structure. This solves the problem of multiple brands of atoms in the hybrid methods. By the brand of an atom we understand different incarnations of an atom of the same element differing by the way it enters in the model: extrema are e.g. Lennard-Jones and some quantum chemical (*ab initio* or valence approximation) atoms. Apparently the former has as attributes relevant Lennard-Jones parameters, the latter - the AO basis. Respectively the atom-based properties (charge distributions etc) when applicable are treated as universally polymorphic lists of attributes.

3 Current Implementations and Future Developments

Systematic development of a library requires significant resources which are normally not available in the context of the grant-based funding supporting projects with narrowly targeted outcome rather methodical development. Nevertheless, following certain programming discipline we could develop enough general and specific procedures and arragne them in the CARTESIUS FORT library. With help of it we could already successfully develop several targeted numeric tools:

- LIQUION - a tool for modeling thermodynamic properties of ionic liquids [39];
- ATOMS - a tool for developing atomic basis sets (solving direct Hartree-Fock and inverse spectrum fitting problems) [40];
- ADAMAS - a tool targeted on description of carbon allotropes which provides their crystalline structures, relative energies and elastic properties [41].

They are for the time being available through the NETLABORATORY system [42]. Further development on the basis of the CARTESIUS FORT library is foreseen.

[2] Values must be supplied by *metadata* including indication to the tensor type of the quantity - $\mathbb{R}$, $\mathbb{C}$, $\mathbb{H}$; rank; space to which the tensor belongs, basis in this space relative to which the quantity is given, units, and mode: whether the quantity is a parameter (input) or result of calculation (output).

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23. "Ferrocene, for instance, may be drawn with the central iron atom connected to each of the two attached rings, to each of the atoms in the rings, to each of the bonds in the rings or not connected at all. The approach taken by InChI is to logically dissociate all atoms capable of forming coordination bonds (metals) and represent the structure as the individual, interconnected components along with the separated, unconnected metal atoms. For a large majority of organometallic compounds, this provides a unique InChI. If a bonded organometallic structure representation is desired, however, it may be specified by adding another series of layers to the InChI." S.E. Stein, S.R. Heller, D.V. Tchekhovskoi, I.V. Pletnev IUPAC International Chemical Identifier (InChI) InChI version 1, Software version 1.05 Technical Manual. Biomolecular Measurement Division. National Institute of Standards and Technology, Gaithersburg, Maryland, USA. However, this InChI does not necessarily represent adequately their electronic structure: a great advantage of the 'classical' structure
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