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Introduction

Chemical bonding: state of the art in conceptual quantum chemistry
An introduction

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Motivation

A most important aspect of scientific progress concerns the development of concepts and schemes, which expand the structured order of the infinite multitude of facts of nature. This requires the design of new concepts which, partly, incorporate previous ones, but which surmount their limits of content, of applicability and of accuracy. The "revolutionary" steps in the evolution [*] of concepts form a continuous process in the history of science. One important part of scientific progress, in addition to generating new empirical facts and new theoretical formalisms, consists of encompassing more details under one common point of view and of inventing new categories of distinction. Another important part of scientific progress consists of didactical classification and of simplification of explanatory concepts for complex phenomenological fields, so that not only experts but also beginners, general scientists and students of general chemistry, and even educated laymen and school pupils can grasp the basic ideas [1]. In these respects natural science is intrinsically interdisciplinary and has relations to the arts and humanities.

Chemistry, or as it is called in China, the Art of Change (*ars mutandi*), originally meant, in the earliest times, the technique of creation of useful and desired properties of foods, colors, materials etc. (Fig. 1). But also, quite early, this art acquired spiritual (alchemical) as well as philosophical bearings, the latter being connected with speculations on the structure of matter in the world. Attempts to reduce the external perceptible properties of macroscopic materials to the inherent basic structural properties of the postulated microscopic elementary particles date back to efforts of ancient Greek natural philosophers; namely, to the ancient form of atomism [2]. It had been proposed that the real properties emerge from the combination and interaction of invisible atomic units. The art of change of matter is then based on the art and science of change of atomic bonding. The conceptual understanding of the chemical bond therefore lies at the center and basis of the science of chemistry.

More naive and less abstract approaches of directly mixing the elementary properties were also developed in early times, including the doctrines of the five elements in China, of the four (or five) elements in classical antiquity or of the three elements in the Middle Ages. Such concepts seemed to be more obvious, impressive and powerful to common sense in most previous cultures, including the Greek one. And they still seem to be so in many cultural circles of modern societies. However, the more abstract and more correct atomistic approach never died out completely [3] and it slowly began its triumph with the empirical justification of atomism by the chemist Dalton starting in 1803 and the physicists Clausius, Maxwell and Boltzmann from 1858 [4]. Two alternative types of concepts of chemical bonding were then developed in competition; namely,

1. The "dualistic" bonding of atoms through electric polar interactions by Davy and Berzelius in 1807 and 1812 and by Helmholtz, Thomson and Kossel in 1881, 1897 and 1916, respectively, and in the following years.
2. The "unitary" interaction of substances, corresponding to what is now called homopolar or covalent bonding, by Dumas and Laurent in 1834/5, further developed by Lewis, Langmuir and Sidgewick from 1916 onwards [5].

The definitive basis of a reductionistic explanation of chemistry, that is, of atomic bonding, of changes of bonding and of the emergence of macroscopic properties and their changes was established through the invention of quantum mechanics by Heisenberg, Schrödinger and Dirac starting in 1925 and by the application of the nonrelativistic part of the theory by early quantum chemists. Nevertheless, the modern concepts of chemical bonding must account, on one hand at least, for the systematics found empirically in previous decades and

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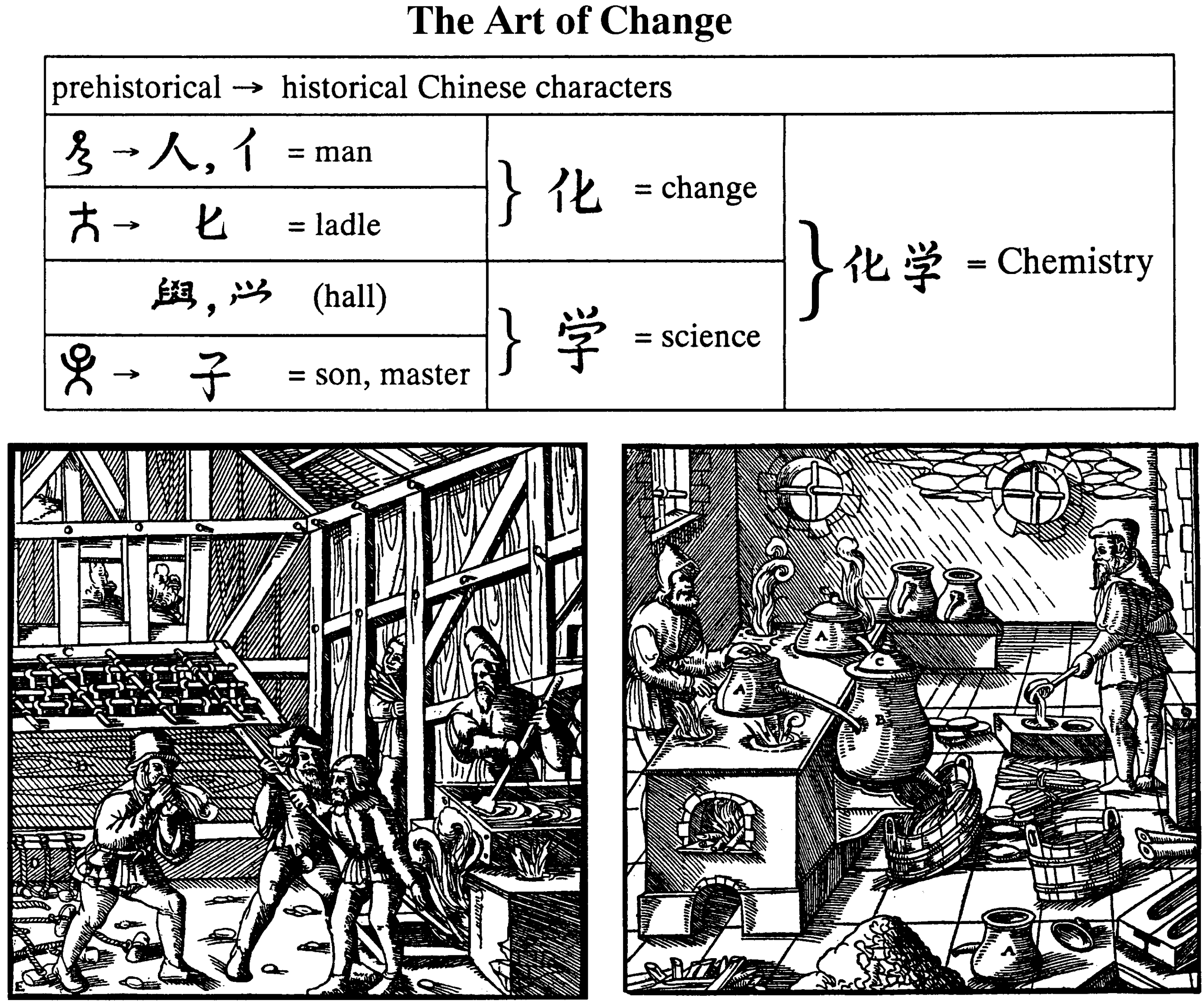

Fig. 1. *Top*: the art of change. *Bottom*: the production of sulfur (*left*) and iron sulfate (*right*), after Agricola, 1556 [14]

centuries by inductive and typically chemical approaches, which are still being extended by further chemical laboratory research. On the other hand, and of course primarily, one has to apply the deductive reductionistic approaches made possible by the modern physical theory of relativistic quantized fields and the respective simplified approximations to it, and one should also try to create new schemes of ordering the manifold of chemical facts along lines which can be assessed by this basic theory. These two aspects of the process of development of chemical concepts might have some relations to the autonomous and reductionistic aspects of chemistry, respectively, though probably not to the ordinary and revolutionary aspects of the development of science, introduced by Kuhn [6].

With this background, a new series of biennial workshops has been established. The first one was recently been organized at La Colle Sur Loup near the French Côte d'Azur by Bernard Silvi (Paris) and János Ángyán (Nancy) together with Carlo Gatti (Milan), Andreas Savin, Mohammad Alikhani and Isabelle Fourré (Paris), Claude Lecomte and Xavier Assfeld (Nancy) and Serge Antonezak (Nice). During the first workshop a set of general problems and fields were vividly discussed [7]. This resulted in refinement of the problems and in the identification of some key questions that will lead to further resolution in forthcoming workshops. Those problems will be posed here without comment, and readers are recommended to consult the subsequent articles. Nearly 30 questions are grouped under eight headings.

1 Quantum mechanical calculation of energies of compound systems

The quantum mechanical calculation of energies is the most common starting point for any investigation of chemical bonding. Traditionally the many-particle wavefunction is at first determined approximately. For many decades, however, it has been known that the one-particle density operator and the two-particle density function alone are sufficient for a direct determination of the nonrelativistic energy. In principle, even the one-particle density function is sufficient (Hohenberg–Kohn theorem). Then there emerge three questions, namely:

1. What would be the prospects of an efficient computational realization of some "one-matrix and pair-density" approaches in competition with the traditional "wavefunction" approaches?

2. Will one be able to develop the "one-particle density", or at least the "one-matrix", i.e. density functional theory approach, into a sound ab initio type procedure, with the option of systematic improvements? And furthermore, how to derive correct operators acting on approximate Kohn–Sham-type wavefunctions for observables which do not solely depend on the density.

3. Which corrections, modifications and extensions are needed to appropriately account for relativistic effects on bonding, i.e. relativistic kinematics and spin-coupling effects, in the previously mentioned two groups of simplified approaches?

2 Physical bond analysis of the results of quantum calculations

In order to gain some insight into the physics of the bonding mechanism, the next step consists of processing and analyzing the calculated wavefunctions and density matrices.

1. Especially simple, easily representable and clearly illustratable functions are the one-particle density in real space and its derivatives such as the Laplacian of the density [8]. These are nowadays generated routinely by quantum mechanical packages and also by the computational tools which generate densities from experimental data, such as multipole refinement programs for electron-beam or X-ray scattering data. Since most information explicitly contained in the many-particle wavefunction and density matrices has been averaged out in the one-particle density, the question arises, what information concerning the bonding mechanisms is still explicitly and obviously manifest.

2. It has also not yet been fully elucidated what additional insights can be gained by analyzing the bond density both in position space and in momentum space or, in the case of periodic systems, in direct and in reciprocal space. At least, the one-electron position density is sufficient to determine the nuclear attraction energy and the momentum density – the kinetic energy.

3. The one-electron density matrix contains even more information. For instance, one can generate the effective one-particle orbitals, generalizations of localized and delocalized orbitals, the electron localization function and other orbital-dependent quantities.

4. Finally, one may also analyze the pair densities, spin-dependent and spin-averaged ones. They offer information on the electron repulsion energy and the electron correlation phenomenon, which contributes large a fraction of the bond energy. And they enable the explicit description of electron pair formation, which is at the basis of the historical bonding ideas of Lewis.

5. Another traditional concept, that of spin coupling, also deserves further elucidation with respect to its meaning for bonding and for bond changing processes.

3 Chemical types of bond analysis

So far we have mentioned only well-defined concepts of the physical kind, based in a surely reductionistic manner on nothing else then the quantum physical equations; however, there are also many autonomous concepts in the chemistry literature which have evolved from chemical laboratory experiences and from less clearly defined chemical ideas. We think here of such concepts as atomic partial charges, electronegativity (dating back to Berzelius [9]), orbital populations, two- and three-center bond orders, aromaticity, reactivity indices and so on.

1. These concepts have an intuitive meaning to the practicing chemist. And there exist operational definitions with recourse to experimental or computational data. For many of those concepts there exist even several different definitions, as in the case of atomic charges and bond polarities, or aromaticity. How can these concepts be put on a more unique foundation? This rather vague question has different aspects; for instance, can one create unique definitions for what chemists intend to understand? Are these concepts one-dimensional or multidimensional, i.e. do they comprise several uncorrelated chemical 'factors'? Etc.

2. There are also many chemical concepts which are different though somewhat related and not fully independent. Examples are covalent and ionic–mesomeric bonding in valence bond theory; or hypervalent, three-center and polar bonding. Which or how many of such chemical concepts are necessary, or at least useful, or superfluous, or even meaningless?

3. Originally, the basic ideas of general chemistry in previous centuries (called theoretical or philosophical chemistry at those times) were rather abstract. At least some leading scientists of the early times of scientific chemistry advocated against concrete visualizations and recommended discussing only the relations between observable properties. After heated discussions over several decades, the concepts of atoms and of atomic structure of molecules and crystals in real space became generally accepted at the end of the nineteenth century. Since then, bonding has been described in real space. After the invention of quantum chemistry, the description of bonding in Hilbert function space, i.e. using one-electron orbitals (or electron-pair geminals), also became popular. Finally, this even occurred in school books, though there the "orbitals" were changed back into regions of real space [10]. So the relations of different bonding pictures in real and in abstract spaces have still to be elucidated.

4 Bonding in finite and in infinite systems

It is common to analyze the bonding of molecules in real space, but that of periodic systems in reciprocal space. The languages and phrases of molecular and solid-state scientists are different and the languages of chemists and physicists also differ. This is partly so because emphasis is put on slightly different aspects.

1. Therefore, further clarification of the differences of bonding in small molecules, in clusters embedded in a surrounding, in nonperiodic extended systems and in periodic, transitionally symmetric systems is still desirable.

2. A special question in this respect concerns the quantum interactions of short and of long ranges between the subunits of small, intermediate and large systems, such as conjugated σ and π couplings in smaller and larger rings, and the mutual perturbations of localized orbitals in finite and extended systems.

3. Concerning the latter "objects", one may ask what the consequences of the different long-range behavior of localized orbitals in typical insulators, in small gap semiconductors and in metals are. This question has two sides. One refers to special physical phenomena, such as the spatial range of neighboring group effects. The other refers to more general aspects. What is the influence of the exponential and the power decay of localized orbitals in insulators and metals, respectively, on local, on nondynamical and on dynamical correlation effects of bonding? What are the consequences of these differences for bonding in the frameworks of valence bond and localized molecular orbital approaches?

4. There exist also other mathematical constructs, especially ones characteristic for periodic structures, such as minimal surfaces. What insight into physical bonding mechanisms do they offer? And can one even develop completely new concepts of bonding, especially adapted to the situations in solids, and less affected by the thinking and preconceptions of physicists or of molecular chemists?

5 Understanding the physical mechanisms of bonding

Some scientists are (already) pleased when they have determined and analyzed the wavefunction of a molecule. Some other scientists, both from chemistry and from physics circles, are in search of something more. These "philosophical heads" are only satisfied if they can achieve some intuitive understanding of the working of the basic physical equations. The following questions are, then, at the border of science and philosophy (or even psychology of scientists).

1. The first type of questions concerns the mechanism of how and why the mathematical Schrödinger or Dirac equation produces, in the underlying physical case, an eigenfunction with the actual density and pair-density distributions and energy components of the atoms bonded in the molecule [11].

2. Another type of question concerns the kind of mathematical quantities which are to be analyzed. One can confine oneself to those observable quantities which are represented by simple linear self-adjoint operators of quantum theory; however, it is also possible to define quantities which are uniquely related, though in a more or less arbitrary manner, to well-defined measurable or calculated quantities. Examples are choosing the ground states of independent atoms as the reference for the molecular energy or electron density or choosing a set of atomic orbitals, which are adjusted by some extremal principle to the molecular state function, as a reference for population analyses.

3. A further common strategy with similar aims is the partitioning of the observable bond or interaction energy into components which may be attached with some physical meaning. There is quite a bit of arbitrary freedom in those procedures, while it is nevertheless difficult to avoid many different contributions of large value and different sign; such complex patterns of energy partitioning would not support intuitive understanding of the physical mechanism of chemical bonding.

6 Classical and quantum bonding

Systems of charged particles are especially sensitive to perturbations by other charged systems. These perturbations are responsible for the breakdown of long-range quantum correlations and the emergence of classical properties.

1. So the basic question arises, where and when do the quantum correlations break down in larger molecules, for instance, as a function of the solvent properties? On what time scales and in which spectroscopic investigations will this show up?

2. A more practical chemical question is how far do the shell models of hierarchical structures not only form simplifying models, but also reflect the real physical situation. We are thinking of shell models, where the central part of the system is treated quantum mechanically, while the environment is represented by a classical, say, a force field, model.

3. The typical thinking of chemists is predominantly classical. Still nowadays chemists often look upon the orbitals as classical objects, such as the bond lines of the classical structural formulas. Nevertheless this approach has brought great progress to chemistry. An impressive example is the chemistry of aromatic compounds in the first third of the twentieth century and also in later years, since the ideas of Hückel and of Pauling and Wheland influenced the classical thinking of the laboratory chemist only slightly. So, where are the real limits of classical pictures of microscopic chemistry and those of molecular chemistry? Here we are talking of the limits of classical phenomenological descriptions, not of reductionistic deductions from basic physics.

7 Changing the bonds

So far we have directed our attention to the description and explanation of the static problem of bonds as they are. The central question of chemistry as the art of change, however, concerns also and especially the bond changing processes.

1. As chemists we not only want to calculate and describe the electronic details of bond breaking and bond formation, but also to understand why physics takes the actual route.

2. Of special importance to the practicing chemist are reactivity indices, which describe the tendency of the molecular ground state to undergo bond changing reactions under different kinds of conditions.

3. In the age of material science, crystal engineering, supermolecular chemistry and sophisticated synthetic arts minor modifications of bonding by the environment are also important and these are decisive for intermolecular interactions in condensed phases and for solvent effects.

8 Philosophical and didactical aspects

In recent years discussions about those aspects appeared in specialist books, for example Ref. [12], as well as in magazines of general chemistry such as *Journal of Chemical Education*, Chim. Didact. or *Chemie in Unserer Zeit*.

1. The previous questions lead us directly into the debate of how far, in which sense and to what extent chemistry, in general, and chemical bonding, specifically, can be reduced to physics. While a lot of heated discussion of chemical reductionism can be found in the literature, it sometimes lacks a sufficiently scholarly treatment of either quantum physical or philosophical or ideological subtleties.

2. A less subtle, though still philosophical, issue is whether there is only one correct, coherent description or explanation of chemical bonding. On one hand, there is only one underlying physics. On the other hand, choosing different gauges of electromagnetic fields, of chemical forces, selecting different explicit forms of perturbation theory and different formulas of multiple perturbation effects and defining different parameters for the bond analysis opens a wide window to very different pictures of bonding. Sometimes these pictures look so different that they are interpreted as contradictory instead of consistent but complementary or even paradoxical.

3. This situation has important consequences of a very general kind. First, one may accept one of the different standpoints of the philosophies of nature and of science which seems to fit best to these experiences. This concerns, for instance, the question of reducibility of chemistry to physics or the uniqueness of the concepts of chemistry as a science of especially complex objects; or how much sense there may be in perspectival epistemologies, etc.

4. Second, chemistry supplies us with the material basis of our existence. This is in significant contrast to the knowledge and attitude of many influential people in society. Among the important members of our community are especially those who teach the new generation. Therefore, it is important to develop pedagogically useful, easily understandable pictures of chemistry and of the chemical bond, not only for the practicing chemist, but also and especially for teachers and for pupils.

5. Especially, it must be discussed at what educational levels and to what extent the concepts based on physical theory, and the concepts based on phenomenological chemistry, should be presented. To contribute a clear overview of the plurality of basic and of simplified concepts, their relations, strengths and weaknesses, is not only an obligation to society, it also seems especially promising in the present age of wide-open information channels. For instance, the recent claims of the observation of orbitals on the Internet and many popular science magazines [10, 13] and the resulting confusion in the science education community should reinforce the respective efforts of scholars.

The diversity of problems and answers posed, given, touched upon explicitly or implicitly during the talks and discussions in the Symposium on Chemical Bonding [7] are relevant to both the scientific community and the general public. These issues should and will be deepened and clarified in the meetings to come. The next workshop of this series is scheduled for Spain in 2002.

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* Here and below we do not follow the beliefs of T Kuhn [6] nor of contemporary intellectual circles of deconstructivists or culturalists.

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