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Author's Review

The Hierarchy of Models in Chemistry

Carl Trindle

Chemistry Department, University of Virginia, Charlottesville, VA 22901, USA

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Chemists make sense of the world with the aid of a variety of models, which may be pictorial, verbal, or mathematical. We develop criteria for useful models and describe in general terms several prevalent models widely used in chemistry. These include the structural formula; classical and statistical thermodynamics; and a variety of bonding models. Finally, we describe the possibilities and potential advantages of encoding the chemist's essentially non — numerical conceptual models of bonding as computer programs according to the methods of Artificial Intelligence research.

INTRODUCTION

In the past decade a new discipline has emerged. The processes by which we develop descriptions of complex systems have themselves become the object of analysis. The descriptions are called *models,* and the development of descriptions is called *model-building.* The terminology carries a number of significant connotations. If we are merely building a model, we relinguish any claim to perfect truthfulness; models are always other than the object being modeled. We stress the tentative nature of the undertaking; models are temporary aids, always to be revised, and eventually to be discarded. Further, we acknowledge the specialized purpose of most descriptions; a model suitable to one purpose will generally be inadequate for other needs. Finally, we now take explicit account of the role of the model builder; the positivistic ideal of a perfectly unprejudiced, unselective observer of nature is set aside. Instead, it is recognized that the model builder has a purpose in mind, which is expressed in the act of model building. To a greater or lesser degree, the behavior of the model is an expression of the consequences of a set of preconceptions of the builder. Paradoxically, this is one of the major advantages of the model-building approach; preconceptions which might otherwise be disguised must be made explicit as the model is constructed.

The popularity of model building outside the physical sciences stems from the work of Forrester[1], who adapted the techniques of mathematical simulation of dynamic systems to social problems. Previously, this computationally demanding approach to complex systems had been applied to engineering problems (chemists are familiar with similar efforts in reaction kinetics). However, the results of Forrester's work, popularized in the Club of Rome Report *Limits to Growth*[2] (Meadows, 1972), had the dramatic effect of imposing a new vocabulary into the debate on the possibility of continuing familiar economic poli-

cies. The discussion of global economic development became an explicit comparison of the results of competing computational models.

At almost the same time the idea of model — building was transforming theories of perception in psychology[3] (Gardner, 1983). Where psychological behaviorism had discarded any hope of authoritative statements on internal mental processes, the *information processing* view of perception offered a picture of the cognitive process as a dynamic interpretation and integration of stimuli. Here again the role of the observer — a model builder constructing an orderly picture of the world from fragmentary data — was given prominence. The information processing view owed much to research in artificial intelligence, which produced on occasion startling behavior from a computer by subtle programming. Construction of the program — a working model — was a primary strategem in AI research, for the test of hypotheses on how best to organize information in a finite system. It was hard to refrain from making the long leap from the demonstration that a computer could imitate intelligent behavior to the idea that human intelligence was the result of a system resembling a computer at least in organization*. The debate in psychology as well as in AI research became increasingly a comparison of the results of computer programs embodying particular assumptions on brain organization. This style of debate even extended to philosophical treatments of the mind/brain problem, though the philosophers did not go so far actually to construct programs, but confined their discussion to Turing machine possibilities (Dennett).[4]

It has also become a part of the protocol in theoretical chemistry to illustrate our assumptions in the form of computer programs, which then provide us an account of the consequences of those assumptions. Much of the vigor in theoretical chemistry can be credited to advances in computer technique and the attendant ease of constructing computer models. We now pose — and answer — questions inconceivable without computer intervention. Computing will effect further change in the type of model preferred in chemistry, just as it has in psychology, economics, and philosophy. We describe a number of currently popular (widely taught and used) conceptual models in chemistry, and use general criteria for effective models to evaluate the models of chemical bonding. We venture some speculations on the models which might replace them. First, however, we will find it useful to develop a kind of taxonomy of models.

I. WHAT IS A MODEL?

Model: (1) an object, usually in miniature and often built according to scale representing something to be made or something which already exists; (2) a pattern, example, or standard; (3) a representation of something later to be reproduced in more permanent material. (Funk and Wagnalls dictionary)

The word *model* is not simply a technical term, but is used in everyday language. It has a variety of connotations, which are worth a brief review. The common feature of all uses of this word is that the model is meaningful to the extent that it suggests or represents something else, which we refer to

* (Of course, it was a well-established tradition to adopt the most subtle and powerful new technology as a picture of the action of our most subtle and powerful organ.)

as the *object* of a model. The model always is distinct from its object, and may be very different from its object in various ways.

The model may be different from its object in scale, as a molecular model, a model airplane, or an orrery*. Such a model is called *iconic;* it resembles its object, as does a mannequin, in a high fashion showroom or a clay model in auto design, but is is not called on to function as its object does. Sharing the form of its object is sufficient, in the examples quoted. The iconic model may differ in dimension from its object. Portraits and maps model three dimensional systems in two dimensions.

A model may resemble its object in behavior as well as form. Such models are called *analogic.* The *working model* required by the US Patent Office in support of claims for new inventions must operate on the same physical principles as its object. In other connections this requirement is waived; if a model behaves in the same way as its object, we often tolerate the possibility that the imitation is superficial. The analog computer models a mechanical system by substituting the behavior of capacitors, resistors, and inductors for the behavior of masses, springs, and dashpots. There is no immediate iconic similarity between the computer model and its object, but the model is nonetheless faithful to its object.

In general, a model need not bear any close physical resemblance to its object. Often all that is required is a similarity in the abstract properties of model and object. Most models are in part or in whole *abstract.* Blueprints bear an abstract resemblance to buildings, which requires some learning to recognize. Linguistic models are even more abstract. Iconic resemblance and even direct analogy is invariably lost in verbal descriptions. Even though there is no obvious resemblance between the marks on a page or the vibrations in a sound wave and a landscape, nonetheless the description permits easy recognition of the object. From language, we construct a model in the sense of representation; a picture in the sense of *Bildung.* The very abstract model of our experience provided by language is highly effective and useful.

II. THE RELATION BETWEEN A MODEL AND ITS OBJECT

It is not a proper goal of modeling to attempt to reproduce every detail of the object. The value of a model lies in its ability to simplify and schematize. A model is less than its object. In this lack of fidelity lies the strength of the model. A good model is not the truth, but a helpful lie. It distorts its object by simplifications, and by giving attention to only selected features. It is in this simplification that the art of modeling may be recognized.

III. PROPERTIES OF A USEFUL MODEL

An artful model is above all useful. Models are to be used. To be useful, a model must be memorable; simple; self-consistent; powerful; and flexible.

Memorable: we use the model to guide our thought, so it should be easy to hold in mind. It should be easy to describe to others.

Simple: If a model is to be useful, it must be *as simple as possible, but not simpler.* It should not incorporate distracting and inessential details, and should contain the minimum number of distinct units. Simplicity is sometimes to be

* a mechanical model of the solar system.

preferred to completeness, though this is always a focus for debate in any special case. The ideally simple model is more memorable than a complex model.

Self-consistent: at the very minimum, a model should not be contradictory. Logical consistency is surprisingly difficult to assure in verbal and pictorial models. This is one major reason for the popularity of mathematical models; they at least embody the logic of elementary mathematics. However even mathematically expressed models can contain contradictions. One should take steps to assure that the model obeys fundamental physical laws; conservation laws and symmetry conditions known to apply to the object system must apply to the model.

Powerful: a model may be powerful in two senses. It is powerful in the first sense if it is very widely relevant, as is thermodynamics, or faithful in great detail, as a portrait. But a model may also be powerful in the more important sense of producing surprises. Of course the properties of a model are in a manner of speaking tautologous. All the theorems of Euclid are implicit in his axioms. Likewise the results of any model are implicit in its construction. But a powerful model will reveal surprising behavior in a striking way. It will render comprehensible aspects of its object which would otherwise be inexplicable and even be overlooked.

Flexible: the behavior of a model should be stable to small errors. It should be easy to make corrections, additions, or more general revisions without shattering the model and forcing a complete reconstruction.

IV. SCIENCE AS MODELBUILDING

Naturally scientists find it easy to recognize their work as a process of constructing ever more desirable models of the behavior of nature. The phrase conveys a degree of humility. No one engaged in building a model can have high pretensions of complete, final understanding of the object of a model. The model-builder admits that his artifact will be limited in application and may even fail unexpectedly and spectacularly. This failure is not looked on as a monumental, disastrous collapse, but as a natural part of the modeling procedure. At least the possibility of failure must be part of the design of the model, or one can never learn anything definite about the object of the model.

A model in science is not simply a description of the object, even though one often hears the expression *statistical modeling* used as a synonym for fitting equations to data. A scientific model exhibits its own properties or behavior, which may resemble some of the properties or behavior of the object. The act of construction of the model is at least as important as its eventual form. Model building requires the identification of a system, which contains items of interest, and its surroundings which may be viewed as a collection of reservoirs. Within the system, one identifies fundamental units whose internal composition is disregarded. These units are ascribed properties, and interact according to laws. The behavior of the system is considered to be dictated by the properties of the units and their interactions. (This excessively general description takes on meaning only when applied to particular problems; the reader is invited to consider any thermodynamic analysis as a more concrete example.) This brief account shows that achieving a mathematical fit to data

is not by itself modelbuilding. The fitting need not even refer to any scientific model, and may be no more than a clerical exercise. If, however, you insist on fitting data to the first order law based on the assumption that radiodecay is a sequence of independent random events — then you are using a model to guide your work.

The most striking feature of the models used in science is their strong overlap and mutual reinforcement. In fact a clear indication of the eccentricity of fringe science is that its views call for the overthrow of well-established scientific principles or make no contact at all with commonly accepted science.

V. THE VALUE OF VERBAL AND PICTORIAL MODELS IN SCIENCE

The vast majority of models in humanistic disciplines are verbal and pictorial. This is true no less in science than in history or philosophy. In chemistry the most prominent linguistic model is the atomic theory of the 19th century and the most prominent pictorial model is the structural formula. When we write a balanced chemical reaction we appeal to the syntax of a linguistic model. Of course there is mathematical (arithmetic) structure in the balanced equation, but the rules for manipulating the fragments in the equation are syntactical. Whenever we sketch a Lewis structure we are relying on the pictorial content to convey or evoke information about the object. It would be quite misleading to say that even theoretical chemistry has dispensed with this type of model. Indeed much effort in theoretical chemistry has been directed toward reconciling the abstract models of matter developed by physicists with the pictures of matter independently constructed by chemists. Examples are numerous, but probably the most determined effort of that kind has been the attempt to reconcile the quantum theory, chemistry's most abstract model, with the picture of the molecule as a collection of atoms linked pairwise by bonds, elementary chemistry's most humble model.

VI. THE VALUE OF QUANTITATIVE OR FORMAL-LOGICAL MODELS IN SCIENCE

Formal, abstract, mathematized models do not typically emerge early in the history of a science (chemistry was a craft surrounded by magical ritual long before it found a quantitative basis). However mathematics (including logic) seems to be unreasonably effective in the description of physical systems and in producing novel predictions. Mathematical models enjoy clarity and may be made free of contradictions, and yield detailed numerical predictions subject to test. However, exact mathematical treatments are generally restricted to such simple systems that their applicability to real systems can be called into question.

Mathematical modeling has been made more convenient and powerful now that computers make possible the treatment of models which cannot be reduced to compact mathematical expressions. Computer models are computer programs, and give a special flavor to debate. The major claims made for computer models are that:

1. Each entity considered significant is explicitly recognized as a variable in the model.

2. The mutual influences of one entity on another are given unambiguous form in the computer code.

3. A quantitative relation — even so crude as the statement that *increasing A requires the presence of B* — must be given explicit expression, and may in principle be tested and refined, or rejected if proved false.

In other words the model (at minimum) serves the purpose of making assumptions explicit and clear, and providing a common basis for discussion. Modeling by computer program is not a panacea; it is subject to the objections that some important features of systems may not be representable by a number. Even where a mathematical representation is proper, so much data may be missing that the model cannot be defined fully or tested in any meaningful way. Complex models are difficult to verify even when they are well defined; simple models may be unable to capture essential features of real systems. Models in physical science do not suffer from these problems to the degree that economic and social models do, but these difficulties plague models of the atmosphere, for example.

VII. THE CHEMIST'S MANNER OF MODELING

Chemistry uses all types of model, iconic, analog, and abstract.[5] (Suckling) The pilot plant is iconic, while the bench scale synthesis is an analogic model of a commercial process. However chemistry is dominated by abstract models; this is one reason for the great difficulty most people encounter in the study of our subject. The most prominent model in chemistry is the periodic chart. Describing this central object of veneration as a model stretches our idea of what a model can be. The periodic chart surely bears no iconic resemblance to physical materials, and is not analogic in its behavior. It is purely symbolic and abstract; its units are the chemical elements, of course, but the relation between the units is rather difficult to state in a compact way. Position on the chart is somehow linked to similarity in any of a huge variety of properties, but the form of the chart does not derive directly from any of these properties except the atomic number. The model is powerful because its form encodes trends in behavior which could hardly be expected without the suggestions of the model.

The second major model in chemistry is the structural formula. This model is partly iconic in its ball-and-stick realization. It is partly analogic, with balls linked by springs playing the role of atoms linked by bonds, sharing a three--dimensional geometry. But it has a large abstract content as well. It is characteristic of models in chemistry that they have developed a rich pictorial content to complement their mathematical abstraction. The strongly pictorial structural formula is the essential model in chemistry and is the common focus of the variety of models in use.

VIII. A HIERARCHY OF MODELS IN CHEMISTRY

Chemistry is recognizable by its effort to represent the behavior of bulk matter as the consequence of the interaction of molecules, and the effort to represent the properties of molecules as the consequence of structure. The idea of a molecular code for genetic information, and (for example) the explanation of sickle-cell anemia as the result of a substitution of one molecule for another illustrates the power of this program. The entire array of models used by chemists is eventually linked to this general representation of nature.

Thermodynamics as a Model

The least detailed model is provided by thermodynamics, in which the units are phases and the interactions are limited to the transfer of heat and energy. Thermodynamics is primarily a mathematical — logical model and its abstraction is only poorly disguised by talk of steam engines. It provides testable, quantitative consequences within its constraints. Further, it provides a common vocabulary for the discussion of phenomena. It is simple in that only a small number of quantities suffice to describe thermodynamic behavior. Its strength is that it does not depend for its validity on the correctness of any particular model of the microscopic nature of matter. This is also its weakness as a model since it is not immediately memorable and has little intuitive appeal. Nonetheless, it is a highly successful model, of overshadowing importance in chemistry. Attempts to make thermodynamics memorable to chemists, however, generally appeal to models of the microscopic structure of matter, eventually based on the structural formula.

Statistical Mechanics as a Model

The laws describing the behavior of bulk matter are assumed to be consequences of the distribution of many particles over accessible states. In the simplest cases, particles are only ascribed masses and move according to Newton's laws. At a more advanced level the particles are assumed to have geometric structure — reflected in the structural formula — which helps to define the states available to the system and the forces acting in the system. In this way statistical mechanics unites thermodynamics and molecular theory. Although it is more mathematically elaborate than thermodynamics it is ultimately more satisfying since it accomplishes the central aim in chemistry of attributing behavior to the properties of molecules.

Chemical Kinetics as a Model

At the purely phenomenological level, chemical kinetics refers only to the phases of bulk matter described by thermodynamics. It extends thermodynamics by introducing the time dimension and acknowledges some properties of materials ignored in thermodynamics, but its rate constants and rate laws need not refer directly to the microscopic scale. Much of the formalism in kinetics has direct analogies in thermodynamics. However it has been the goal of most kinetic investigations to rationalize the behavior of bulk matter by reference to properties of individual molecules. Correspondingly the formalism of microscopic kinetics has been adapted from statistical mechanics, and ideas strictly applicable only for bulk systems at equilibrium in the statistical thermodynamic model have been adapted to small systems far from equilibrium. The most popular of these models has been the absolute rate theory of Eyring, which still dominates the vocabulary of description of rate processes.

The Mechanism as a Model

The statistical mechanics and chemical kinetics call up pictures of individual molecules encountering one another and in the course of the collision

exchanging energy and sometimes altering structure. There is little obvious mathematics in this essentially pictorial model. The details of the motion have been deduced from more formal analysis of numerical data. Stiffness or frangibility of bonds have been translated by the chemist into the resistance of the molecule to various types of deformation, upon collision. This chemical view has more in common with sculpture or dance than mathematics or formal logic.

The Structural Formula as a Model

Chemists find explanations referring to properties of molecules most convincing, and have developed a powerful code for molecular properties, in the structural formula. Given the structural formula, a chemist can deduce a variety of properties of the substance so represented, including melting and boiling temperatures, color and other spectra, and general patterns of chemical reactivity. The structural formula does not contain or model this information in any obvious way, but rather serves to evoke such information from the experience and theoretical training of the chemist. The structural formula plays a greater role as a medium of expression and an aid to memory than as a model, but its humbler role as a model is still important. Certainly the effort to visualize three-dimensional structures would be much harder without it, and chemists from van't Hoff and LeBel to James Watson owe much to geometric *iconic* objects.

There is a subtler sense in which the ball and stick is a model. It makes concrete our presumption that the molecule has the property *shape*. It is worth noting that shape is a property of bulk matter; it is a classical idea, summarizing much of our experience at the human scale. Much recent debate has attended Woolley's suggestion that this idea may in fact lose its validity in the realm of single molecules.[6,7] It is surely the case that most of our bonding models accept the idea without question.

IX. BONDING THEORY AS AN EXERCISE IN MODEL BUILDING

Theoretical chemistry has as its major role the refinement and rationale of the fundamental chemical model, the structural formula. Features attributed to the molecule, coded into the structural formula, are to be recovered from the bonding theorist's model. The object in bonding theory is to explain why some atoms bind together and others don't; why compounds have their particular composition and not others; why some compounds are long lived while others are unstable; why some compounds have a common elemental composition yet different physical and chemical properties.

Bonding models satisfy these requirements to varying degrees. The earliest systematic model in chemistry owed much to alchemy and the idea of *elective affinities*. The model suffered from vagueness and a low (though not zero) power of prediction. Dalton's atomic theory, with the mass scale established by Cannizzarro and the convenient notation devised by Berzelius was a necessary predecessor to the geometric models devised by van't Hoff and LeBel. These models explained in a convincing way the variety of isomers found among chemical species.[8] However, these models evaded the question of what constituted the bond. A more successful and general model would establish

a link between stereochemistry and the physicists' picture of matter as composed of charged species.

The Bohr atom constituted the first physical — mathematical model for the periodic table, and introduced the idea that there was a link between the arrangements of electrons in atoms and the chemical properties of elements. The first models to acknowledge the electron theory of matter did little more than count the electrons and classify them as chemically active (valence) and inert (core) electrons. Even with this simple picture of matter the Lewis model predicted chemical formulas and established a connection between the disposition of electron pairs between nuclei and the bonds between nuclei. Gillespie[9] extended this model to accommodate the mutual repulsion of electron pairs and were able to reproduce the geometry of molecules as a consequence of their valence electron pair repulsion models. These strongly pictorial models still play a key role in the initiation of novice chemists.

The picture of the molecule as a set of slow moving nuclei in an electron distribution was to be the basis of more abstract models of bonding. The Born--Oppenheimer approximation[10] simplified the quantum representation to a rigid lattice of charged mass points; these defined the field in which the electrons move. The mathematical problem was still so difficult that approximations — a form of model building — were required. The valence — bond description took the chemist's picture as the most appropriate basis for a model, and enjoyed considerable success[11]. It played the critical role of a model in chemistry, as defining a common vocabulary and providing a compact pictorial notation. It is still dominant as the rationale behind the electronic (resonance) theory of organic chemistry, even though its limitations are now common knowledge.

The molecular orbital theory took the individual electron in the nuclear field as its primary unit, and displayed unparalled power in the description of spectra and magnetism. Its qualitative, pictorial aspects are now part of the arsenal of the chemist. Typically, the qualitative features of orbitals and the vocabulary of the theory are all that most chemists find useful. And of course its popularity blossomed only after convincing, simple, and uniquely powerful applications were developed by Mulliken in spectroscopy[12], Walsh in molecular structure[13], and Woodward and Hoffmann for reactivity[14]. The striking feature of both valence bond and qualitative molecular orbital theory was that they were acknowledged to be flawed, incomplete models of a more complex model, which was inconvenient to treat directly. Far from considering this a shortcoming, we should realize that the oversimplifications resorted in early applications of the molecular orbital theory (perhaps out of desperation) were instead the strengths of the models. More realistic, more complex models would not have made such an impact. Most »improvements« to these early models met with stony indifference, since they sacrificed the simplicity and pictorial clarity of the first models.

X. MO PROGRAMS AS MODELS

We will find it helpful to consider the proliferation of approximate MO packages to be variants on a single model. The units of the model are cores and valence electrons. The interactions among units are not quite the Coulomb interactions, but a simulation. Within the SCF formalism, these interactions are represented by integrals' numerical values. The Coulomb force — an im-

portant feature of the Hamiltonian model of the molecule — is represented by integrals in the Hartree — Fock model. These integrals are assigned values so to modify the performance of the still simpler MO models. The various models are modified so to mimic various measurements, including heats of formation, frequencies in the optical spectrum, or the computational results of more elaborate models. When these theorems still apply, the model is judged by its satisfaction of the virial theorem and the variation principle.

Much of the discussion of the value of models derived from the Hartree--Fock equations has been focussed on their quantitative results. A broad range of behavior consistent with independent observations will naturally strengthen the reputation of a model. However our discussion suggests that other criteria be used in judging the value of a model in addition to its ability to mimic known behavior.

Are these models memorable? No, to all but their maker, these computer programs are black boxes.

Are they simple? Yes, in comparison to the larger calculations from which they derive. But no, not if the objective is to hold the model in mind and use it as an aid to thought as one can use the structural formula.

Are these models at least self-consistent? Much effort has been expended to assure that symmetry is maintained in the computations, but special steps had to be taken to assure rotational invariance, invariance to choice of energy reference point, and proper scaling. The models must still suffer from the symmetry dilemma of their (open-shell) Hartree-Fock object, and suffer from its failure to establish proper spin symmetries.

Are these models powerful? They have a potential for very broad applicability, since one can formulate an expression for any molecular property for which a quantum mechanical operator is defined. In practice their utility is limited largely to estimating properties similar to the data used to calibrate their parameters. While this is far from trivial, we must also ask whether these models are powerful in the second sense: do they produce informative surprises? Here their record is not distinguished, despite occasional successes. It may be that approximate MO calculations support or deny speculations on bonding, transition state structure and therefore serve a useful purpose, but as a source of new ideas their performance is not remarkable. These speculations are generally based on much simpler pictorial models and ideas such as hybridization, overlap, approximate local symmetry, or electronegativity. The approximate MO models serve the valuable role of governors of otherwise undisciplined imagination, which works with these qualitative ideas.

Are these models flexible? A useful model should be easy to extend or revise, and it should not be sensitive to small errors in parameters. Semi-empirical MO programs are tied strongly to the minimum basis set, restricted Hartree-Fock formalism. Extension of the programs to incorporate configuration mixing or other amendments generally requires starting over. I do not know of systematic sensitivity analyses of semi-empirical MO results with respect to choice of parameters, though this is a common feature of mechanistic modeling in chemical kinetics, and must have been done in the course of choosing parameters.

We are driven to the conclusion that the commonly available *ab initio* and semi-empirical MO programs have few of the generally desirable features of models. They are a compromise between the true and the simple, as all models are, and may not be true enough to excuse their lack of simplicity and flexibility. In the eyes of most chemists, they suffer from obscurity, inconvenience, and unreliability.

XI. THE NEED FOR QUALITATIVE, PICTORIAL MODELS IN BONDING THEORY

A number of theoreticians have devoted effort to the task of translating the rather inaccessibly abstract computationally clumsy quantum mechanical models of molecules into semi-quantitative models. These efforts take several paths.

One may attempt to invent new qualitative descriptions of the quantum mechanical results on the basis of energy density.[15]

Representations of bonds, atoms, and lone pairs have been recovered from single determinant wave functions[16,17] and from more general electron density functions[18]. MO computations may begin from bond and lone pair functions strongly resembling links and nodes of the structural formula.[19]

One may look beyond the quantum mechanical foundation and construct quantitative models of the qualitative ideas which have been the enduring product of highly approximate calculations. Prominent among these are the maximum overlap model[20] (Maksić), the quantitative PMO model[21] (Wolfe, Hwangbo), and valence bond models[22,23].

One may discard any reference to the quantum mechanics and deal more directly with the structural formula. Molecular mechanics has been very successful as direct translation of the mechanical properties of the physical iconic molecular model and the spectroscopic semiclassical model[24].

The structural formula has also been considered as a graph[25]. Even though the graph discards much of the information important to the chemist's use of the structural formula, the graph theory permits some remarkable generalizations on the properties of the represented molecule[26]. One particularly interesting use of the graph is to arrive at a refined expression of the *complexity* of a molecule[27]. Complexity is a typical chemical model concept like strain, synchronicity, or electronegativity, in that it seems to carry a particular and clear meaning, which meaning seems to dissipate on close examination.

I believe that there is an opportunity to use the techniques of mathematical modeling to improve and refine chemistry's central model, the structural formula. It seems to me reasonable to construct models of molecules free from the quantum mechanics, as has been done in molecular mechanics. The purpose of such models will be to make explicit (and therefore testable) most of the properties we attribute to the structural formula. Model building in which these properties are made explicit can expose any inconsistencies or contradictions in our everyday use of the structural formula. Such model-building will be different from essentially complementary attempts to discern features of the structural formula in the quantum mechanical descriptions of molecules. The new models must resemble chemists' conceptual models, with strong em-

phasis on qualitative and pictorial features. At the same time the sometimes vague and perhaps even not fully recognized properties of the structural formula must be represented unambiguously. These demands are no different from the usual computational requirements that a special language is called for.

XII. A SUPERIOR MODELLING LANGUAGE — LISP

Chemical conceptual models are essentially qualitative and pictorial, and chemical thought requires the recognition of broad similarities rather than perfect identities. Current computer models in chemistry are expressed in quantitative mathematical terms, due to the constraints of most computer languages. The translation of the views of a chemist into numerical form is difficult, which renders the realization of FORTRAN models rather awkward. LISP, the universal language of artificial intelligence research, stresses relations rather than quantities, and thus is much better suited to the modeling of chemical ideas. Its fundamental operation is not the assignment of a numerical value, but the construction of a connection between objects[28]. LISP enables the easy expression of set-theoretic ideas, the representation of natural languages, and the construction of nested relations. It permits — even demands — recursive descriptions, which is much closer to the synthetic chemist's view than is the linear descriptions typical of most mathematical descriptions of chemistry.

XIII. AN EXAMPLE OF A LISP MODEL

We have described a LISP intepreter of structural formulas which accepts sketches from a graphics tablet and assembles of collection of bond lengths and angles[29] (C. T r i n d l e and R. G i v a n, in: *Chemical Applications of Topology and Graph Theory,* Elsevier, Amsterdam, 1983). The program then produces an approximate molecular geometry as input for a molecular mechanics or molecular orbital program. The program relies on the recognition of NEIGHBORS of particular ATOMS in the sketch, and refers to stored values of recurrent bond lengths and strengths in common molecular FRAGMENTS. The FRAGMENTS may be assigned any other relevant PROPERTY, such as chromophore frequencies for representation of spectra, reactivity, Hammett constants, or acidity constants. The capitalized names are the fundamental data structures, and are composed of LISTS, the characteristic manner in which irreducible units (ATOMS) are stored in LISP. As an example, we describe how our LISP representation of the structural formula can be used to codify heats of reaction according to the bond-energy representation. The simplest bond-energy model would associate a parameter — the bond energy — with each neighbor of a particular atom. (A more detailed model would recognize that the NEIGHBOR list of each of the NEIGHBOR atoms would influence the bond energy, but we defer this refinement for simplicity of discussion.) The calculation in its mathematically simplest guise amounts to no more than adding up parameters for each recognizable bond in the reactants, and subtracting away parameters for each bond in the products. No chemist would do this if the reactant and product were generally similar; instead she would add up energies for each bond broken and subtract energies for each bond formed. We can accomplish this within our program by preparing a list called BROKEN of NEIGHBOR — related ATOM pairs present in the reactant but not in the product, and a similar list called FORMED, and confine

our calculation to these generally smaller lists. This rather trivial example serves to illustrate our general strategem, which is to prepare programs which accomplish calculations or eventually judgements by means similar to human judgement. Our approach will be then to subject these models of human chemical reasoning to severe tests to see where intuition fails. We will then have identified general areas of weakness in the chemist's qualitative models, and fruitful topics for further examination.

XIV. A LISP MODEL OF THE QUALITATIVE MOLECULAR ORBITAL THEORY

It is a common practice to use qualitative and pictorial models of bonding, within the general framework of the MO theory, to discuss details of molecular geometry and reactivity.[30,31] These discussions are accompanied by sketches which exaggerate and simplify the values and relative signs of MO coefficients. The actual MO contours computed by the MO computer models often are not so revealing as the sketches. Even though the computed results are more accurate than the sketches, the sketches have an advantage typical of conceptual models that they stress the subtle but critical details of the MO's guiding the effects of interest. LISP modelling can faithfully follow the conceptual modelling. Our functional fragment representation in LISP of the structural formula permits the storage of any property for each fragment, and it is a rather simple matter to assign the relative phases of pi MO's within certain fragments. The qualitative analysis of for example substituent effects requires no more than the phase patterns of fragment MO's, and a rule for their mixing. In the LISP model, as in the conceptual picture, detailed numerical values are not any part of the first impression of the system. Often the computed numerical results are not sufficiently trustworthy to add much value to the analysis (without very detailed, laborious calculation). A rough but pleasing picture often emerges at the purely qualitative level, and the detailed calculation merely refines our expectation. The point here is that the analysis of the detailed calculation is guided by our expectations, which were formed with the aid of the pictorial model. Coding the pictorial model will have the usual salutary effect, of forcing the explicit and consistent application of assumptions in the qualitative model. It will therefore be able to expose internal contradictions in the conceptual model, or direct attention to cases where the qualitative model is ambiguous. Here the detailed numerical models will find fruitful application. Technical details of the program, and representative results are to be described elsewhere.[32] (Trindle, 1984)

XV. ARTIFICIAL INTELLIGENCE AND CHEMICAL THOUGHT

Turning the power of LISP to encoding the patterns of human thought and thereby making explicit the models guiding chemical judgement in particular is far from being a new idea. One of the signal successes in artificial intelligence research[30] (Lederberg) was just such an effort, in which the methods by which experts arrived at a chemical structure from mass spectrometric and NMR data were incorporated into a program, DENDRAL. A more recent similar success was described for chemical reactivity[33] (Jorgensen). Many similar opportunities exist, and are worthy efforts. The results of such research will not only produce useful »expert systems«, but will give deeper

insight into our own modes of thought. Such insight will surely sharpen and improve our models of chemical behavior.

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SAŽETAK

Hijerarhija modelâ u kemiji

Carl Trindle

Dan je pregled modelâ u kemiji, počevši od klasičnih strukturnih formula i statističke termodinamike pa do čitave palete raznih kvantnih modela kemijske veze. Konačno, razmotrena je mogućnost kodiranja kemijskih koncepcija i kvalitativnih modela s pomoću metoda umjetne inteligencije.