Springer | CHICAGO JOURNALS

Philosophy of Science Association

http://www.jstor.org

How the Models of Chemistry Vie

James R. Hofmann

California State University

1. Introduction

   Recent work by historians and philosophers has called attention to the complexity
of modern experimental physics and its intricate relation to interpretive and explana-
tory theory (Franklin 1987, Hacking 1983, Galison 1987 and 1989, Pickering 1984
and 1987). One point of general agreement has been that the contexts of discovery
and justification often significantly overlap and do not uniformly correlate with ex-
periment and theory. Instead, intended applications, instrumentation, experiment, phe-
nomenological description, explicative models, and explanatory theory all act both as
incentives and as constraints during the production of scientific knowledge. The pre-
sent paper investigates how one node of this network operates in the domain of solid
state physics and chemistry. In particular, a case study analysis of how models func-
tion in transition metal oxide research provides ample support for several conclusions.

   First, it must be emphasized that the term "theory" can have misleading connota-
tions in this domain if it is allowed to imply a single and foundational level of ex-
planatory generality. Many modes of nonexperimental activity actually take place;
these include preliminary stipulation of phenomena, determination of quantitative re-
lationships in the form of phenomenological or semi-empirical laws, construction of
causal and heuristic models, and demonstrations that these results do or do not fall
within the explanatory scope of one or another approximate application of the
Schroedinger equation. Each of these efforts receives sustained attention from solid
state physicists and chemists.

   Secondly, with these complications in mind, the distinction between data and phe-
nomena, as recently drawn by Bogen and Woodward, provides a valuable analytic de-
vice to extend Nancy Cartwright's discussion of phenomenological and foundational
laws (Bogen and Woodward 1988, Woodward 1989, and Cartwright 1983). For exam-
ple, much of the progress in the study of transition metal oxides since the 1930's has
depended upon increasingly accurate phenomenological modelling. This practice dif-
fers both from the production and presentation of experimental data and from the
search for explanation grounded upon a more general theoretical basis. A simple di-
chotomy between theory and observation thus is inadequate analytic vocabulary; the
data-phenomena distinction helps define the domain in which modelling takes place.

Finally, the dual function of modelling as the culmination of phenomenology and the commencement of explanation suggests that the evaluative criteria for models will not be uniform. Those solid state chemists and physicists who concentrate on the description of phenomena pertinent to specific elements or compounds will assess models according to different standards than those who seek explanation grounded in approximate applications of the Schroedinger equation. Disagreement about the relative importance of specific causal scenarios and unifying explanatory formalisms thus arises in materials science in a manner parallel to similar debate within the social and biological sciences.

2 The Hierarchy of Theory in Solid State Physics and Chemistry

Virtually all aspects of molecular and solid state physics and chemistry were of course revolutionized by quantum mechanics at the end of the 1920's. Thereafter, in principle, the ultimate explanations in these domains should be provided by the Schroedinger equation applied to the appropriate Hamiltonian. In practice, even the simplest real chemical problems required the creative invention of approximation techniques. A brief historical survey of the most influential of these methods will serve as an introduction to the context in which Cartwright's discussion of phenomenological laws and models becomes relevant.

At the atomic level, Douglas Hartree's 1928 self-consistent field method was based upon the technique of calculating a one-electron wave function by approximating the atomic field as a central, spherically symmetric field produced by the nucleus and the averaged space charge of the other electrons. Following Fock's introduction of determinantal functions to calculate antisymmetric wave functions, the Hartree-Fock method became a powerful technique of great generality; by the end of the 1930's it had produced results close to experimental values for the lightest and least complicated atoms. More specific techniques were devised by Heisenberg and Hyllerass for helium, and Heisenberg's method of calculating electronic wave functions as linear combinations of the wave functions of the two individual helium electrons was particularly influential.

In the molecular domain, in 1927 Heitler and London used Heisenberg's technique as a model to calculate approximate molecular wave functions for hydrogen electrons as products of atomic wave functions. Wave functions calculated in a similar manner for more complex molecules yielded appreciable values only near atomic or ionic positions and thus were particularly accurate for molecules with relatively large interatomic distances. At approximately the same time, Hund developed an alternative "molecular orbital" method very similar in approach to that of Hartree and Fock for atoms. During the 1930's Hund, Mulliken, Lennard-Jones and Huckel applied this self-consistent field approximation to achieve a primarily qualitative understanding of the smallest and least complicated molecules. Since in this approach the electronic wave functions have appreciable extension throughout the molecule, the molecular orbital approach became an incentive for an analogous itinerant electron theory of metals.

This process was initiated by Sommerfeld's 1928 free-electron approximation. Bloch, Bethe, Peierls and Wilson then developed an increasingly accurate band theory based upon the central assumption that the interactions between delocalized electrons could be taken into account indirectly by incorporating them into a representation of the ionic lattice of the metal. The delocalized conduction electrons were described by one-electron wave functions, products of a free wave and a function having a period equal to that of the lattice. Based upon this model of metallic structure, both Bethe's study of X-ray diffraction and Peierls' analysis of periodic potentials showed that the

allowed electron energies fall into bands separated by forbidden gaps. Metals and insulators thus could be distinguished according to whether or not the highest energy band is partially or completely filled.

Wigner, Seitz, Slater and Herring all developed methods to carry out approximate energy band calculations in specific circumstances. The Wigner-Seitz cellular method, Slater's augmented plane wave method and Conyers Herring's orthogonalized plane wave method thus constituted a set of procedures which were carried out with greatly increasing precision after 1951. This was due both to the interest generated by the Shelter Island meeting that year and the increasingly sophisticated computer resources available to theorists such as the MIT Solid-State and Molecular Theory Group directed by John Slater. Transition metal oxide anomalies such as the insulating ground state of nickel oxide thus provoked attention and fostered debate about the legitimate scope of energy band calculations.

During the same period in which these and other approximation techniques went into circulation, experimentalists continued to analyze data using less foundational semi-empirical or phenomenological relationships. For example, transport phenomena such as thermal and electrical conductivity and Hall effect mobility were investigated under a variety of temperature and pressure conditions both for pure compounds and for a wide range of impurity doping. Industrially employed physicists in particular often were more concerned with the practical application of relatively simple relationships than with approximate derivations from more basic principles.

In 1967 several influential theorists took stock of the situation in quantum chemistry. The occasion was the inaugural issue of *The International Journal of Quantum Chemistry*, promoted by three prestigious Honorary Editors: W. Heitler, John Slater and Robert Mulliken. Per-Olov Lowdin, prominent member of the Editorial Board and Slater's close colleague as director of the Quantum Theory Project at the University of Florida, wrote two introductory essays for the first issue. In the first he stipulated the topics to be covered by the *Journal*, and in the second, illustrated by a diagram, he discussed the hierarchy of theory in the field (Lowdin 1967, pp. 9-11).

In a discussion of quantum chemistry one should remember that various types of theory are constructed for different purposes. ... For larger systems, it may be practically impossible to carry through the computations, and certain quantities in the theory may then instead be estimated from observed data whereas others are neglected 'as being small'. In this way semiempirical theories have been constructed which are often highly accurate and useful within the domain for which they have been designed, but which break down completely outside this domain.... In reality all 'theories' are tools for correlating one set of experimental data with another set, and theories of various types are essentially unalike in that they correlate data of different orders of magnitude. ... It is obvious that the use of experimental data available in a field may provide valuable guidance for the development of the theory, but it is more seldom realized how *difficult* it is to utilize experimental information properly. The construction of meaningful semiempirical theories is therefore one of the most important future goals for applied quantum theory, but in the meantime, the existing theories will have to live side-by-side.

Lowdin's explicitly stated instrumentalism with respect to theories acts as a basis for his concern with issues quite distinct from debate over fundamental ontology. The creative invention of semi-empirical laws and the resolution of conflicting implications of alternative approximations strike him as more important projects; his com-
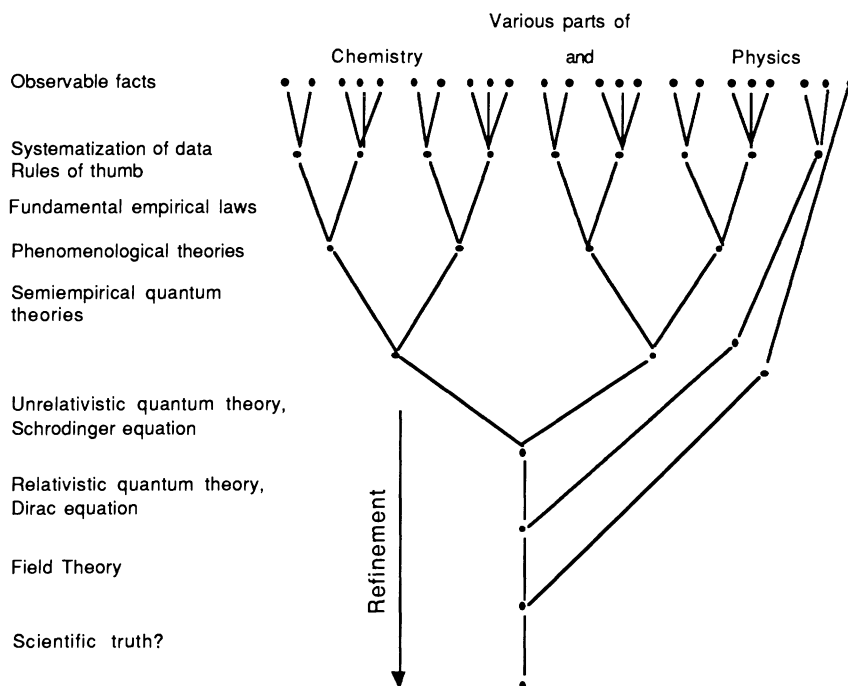
Schematic diagram of the hierarchy of theories concerning the structure of matter, showing the increase of correlated areas of observable facts with the refinement and deepening of the basic principles.

(after Lowdin, 1967)

ments thus lead us to expect lively debate on these topics among solid state chemists and physicists.

For example, the comparison of alternative approximations was a major theme in Frederick Seitz's influential 1940 text *The Modern Theory of Solids* (Seitz 1940). Seitz repeatedly juxtaposed the implications of the Heitler-London approach with those of band theory. The former is particularly applicable to the study of cohesive forces in ionic crystals; band theory is preferable for the electrical conductivity of metals. Nevill Mott, in his generally favorable review of Seitz's book, argued that since

> most of the research workers who are working on solids at the present time are not doing so with any hope of discovering laws of a fundamental kind,.... it seems to me more worth while to attempt to correlate observed phenomena and to give a general explanation in terms of atomic physics, than to attempt any sort of quantitative explanation of phenomena so complicated as those that occur in solids. (Mott 1941, p. 623),

Mott's only criticism of Seitz's book thus was that "it is difficult to separate the important and suggestive theories from the superstructure that has been built on them in the attempt to get quantitative agreement with experiment" (Mott 1941, p. 624).

Mott's view that in solid state theory "a fact is only worth explaining if it can be explained simply" (Mott 1941, p. 624), brought him into direct conflict with John Slater during the 1950's. Slater spelled out his position in an introductory essay for the first issue of the *International Journal of Quantum Chemistry*. After an historical survey, Slater drew a distinction between what he called "a priori theory" and semi-empirical theories which rely upon empirical parameter fixing.

This semi-empirical type of theory obviously has its place, and it is practically necessary if the experiments are to proceed, for they need the guidance even of an imperfect theory to find their way through the complexities of the phenomena which are now being studied.

Slater's worry was that "it is altogether too easy for an uncritical generation of workers to grow up, trained in these half-satisfactory methods, and to think that they are the fundamental laws of nature" (Slater 1967, pp. 93-94).

There are at least two points of ambiguity in Slater's remarks. First, although his term "a priori theory" implies exact application of the Schroedinger equation, he actually had in mind one-electron approximation techniques based upon extensions of the Hartree-Fock approach. This was characteristic usage on Slater's part; for example, in a 1968 review article for *Physics Today*, he commented that the approximate energy band calculations of the 1930's were "the first serious attempt to understand the electronic properties of real crystals in terms of calculations from first principles" (Slater 1968, p. 51).

Secondly, Slater's allusion to the "complexities of the phenomena" represents a complication hidden by Lowdin's reference to the "data" to be correlated by theory. Lowdin's terminology smacks of the theory-observation distinction beloved of logical positivists. By simply offering greater scope or order of magnitude as factors that stipulate a theory's position in his hierarchy, Lowdin obscures the function of the centrally located semi-empirical laws. Regardless of their disagreement concerning the importance of fundamental theory, Mott and Slater share a respect for the heuristic or exploratory value of semi-empirical theories. But they also distinguish these relationships from "laws of nature" which they at least take to be of far greater generality. Before turning to a specific example, the mutual status of data, phenomena, models and explanatory theories needs to be clarified.

3   The Modelling of Phenomena

In the same introductory issue of *The International Journal of Quantum Chemistry* in which Lowdin's and Slater's remarks appeared, Honorary Editor W. Heitler made the following reflection concerning his 1928 approximate calculation of hydrogen molecule bond length.

The purpose was to *understand* the *phenomena* of chemistry and to reduce them to the laws of the newly created atomic physics. Numerical accuracy is less important for this aim than an overall understanding of the rules which govern the forming of chemical compounds, above all the fact that a homopolar bond exists at all, and that this has the typical saturation property of chemical valency (Heitler 1967, p. 14).

Heitler's emphasis on the attempt "to *understand* the *phenomena*" is not casual or accidental. It reflects the central importance of the simplified but useful representations of molecular structure provided by models. Heitler's point is that although the approximate calculations based upon these models are valuable and represent the only practical way to apply the Schroedinger equation, models are even more valuable due to the structural understanding they provide about the causes of molecular phenomena. The work of Nancy Cartwright, James Bogen and James Woodward is particularly appropriate to amplify Heitler's comment.

In *How the Laws of Physics Lie*, Cartwright gives a compelling account of the functional divergence between the descriptive accuracy of phenomenological laws and the explanatory scope of more fundamental theoretical laws (Cartwright 1983). In close accord with the vocabulary of scientific practice, Cartwright stresses that this distinction does not parallel a longstanding philosophical demarcation between the observable and the unobservable. For example, there are phenomenological laws that relate electrical conductivity to the effective mass and mobility of electrons, a relationship which makes specific reference to properties of the unobservable atomic structure of solids. For Cartwright, scientific truth is to be sought in the content of phenomenological laws; their justification is based on the experimental data they summarize and the predictive power they generate. The tendency for accurate phenomenological laws to include assertions about individually unobservable or "theoretical" entities such as electrons, polarons, excitons or phonons is justified by the fact that these laws provide the causal knowledge needed to successfully alter phenomena or produce new effects. Nevertheless, the explanatory power of these laws is restricted in that they primarily describe relatively specific circumstances and do not locate their subject matter within a pattern of related phenomena.

For example, in a 1955 paper James Bierlein explicitly cited his results as a "phenomenological theory of Soret diffusion" (Bierlein 1955). He provided practical approximation techniques for the analysis of a partial differential equation that accurately describes the flux density in a Soret cell in terms of thermal, stoichiometric and geometric parameters, but he did not claim that this equation exemplifies more general principles.

On the other hand, explanation, in Cartwright's sense, must come through the demonstration that the phenomena in question, when appropriately modelled or "prepared", fall within the set of models to which a specific theoretical formalism applies. She takes an instrumentalist position with respect to these formalisms; while their relative generality allows them to bring a variety of phenomena within an explanatory umbrella, this very feature means that they can be applied only to models which to some extent have idealized or approximated the details expressed in phenomenological laws. In this sense, the fundamental laws of physics "lie" in order to explain.

In quantum theory, of course, the formal statement of the Schroedinger equation requires a manageable Hamiltonian for its application. Cartwright's comment is worth quoting (Cartwright 1983, p. 139).

It is no theory that needs a new Hamiltonian for each new physical circumstance. The explanatory power of quantum theory comes from its ability to deploy a small number of well-understood Hamiltonians to cover a wide range of cases. But this explanatory power has its price. If we limit the number of Hamiltonians, that is going to constrain our abilities to represent situations realistically. This is why our prepared descriptions lie.

Cartwright's instrumentalism concerning foundational theory and her realism concerning unobservable entities coincides with the views of practicing quantum chemists such as Lowdin. Given the pervasive nature of the instrumentalist-realist debate in modern philosophy of science, it is not surprising that this has been the focus of some reactions to Cartwright. Ronald Layman, for example, correctly argues that when experiment underdetermines theory, a disparity between phenomenological law and approximate derivation from theory does not in and of itself indicate the false nature of theoretical premises (Laymon 1989). On the other hand, a significant number of solid state chemists and physicists would interpret an increasingly accurate series of approximate derivations of phenomenological laws as an indication of the utility rather than the truth of theoretical formalism. The interrogatory, "truth ?", at the bottom of Lowdin's diagram symbolizes an essentially instrumentalist search for explanatory "foundations". This means that the ontological content of models gives them a pivotal role that merits close attention.

From Cartwright's point of view, models marshall or "prepare" what is known about phenomena into a form amenable to approximate mathematical treatment by the formal apparatus of a theory. Baldly put, this means that "the model is the theory of the phenomenon" (Cartwright 1983, p. 159). More accurately, models have two closely related tasks. They must depict the causal relationships essential to phenomena, and they must represent these relationships in a form that makes clear how theoretical formalism is to be applied. In particular, the second task often must include the stipulation of the relevant approximation techniques needed to bring theory to bear on the case at hand. From this point of view, we should expect that progress will in many cases consist of models vying for success according to these two criteria, and this is indeed what we frequently find in solid state chemistry.

One commendable aspect of Cartwright's account thus is its close conformity to the hierarchy of nonexperimental practices recognized by quantum chemists. But due to the wide variety of modelling techniques, the relation between phenomenological laws and models is not easy to characterize in general. In anticipation of specific examples, the modelling process should first be distinguished from earlier stages in the analytic process, stages which pertain to experimental data rather than phenomena.

In two recent papers, James Bogen and James Woodward have pointed out the detrimental effects of relying upon the traditional philosophical dichotomy of theory and observation (Bogen and Woodward, 1988 and Woodward, 1989). They advocate a distinction between data and phenomena based upon different respective roles in scientific reasoning. In short, data provide evidence for the phenomena that theory explains. The full complexity of experimental data is never actually explained by theory. This is because data are idiosyncratic with respect to experimental equipment, materials and conditions - all factors left unaddressed by theoretical formalism. Furthermore, attempts to replicate experimental procedures result in data with values that vary over some range; the complexity of the causal factors in any interesting experiment make it impossible to explain the exact data resulting from any specific trial. Instead, data provide evidence for the existence of phenomena. Phenomena are inferred from data and have a stability that can be expressed through a variety of different types of data. Since phenomena often involve unobservable processes such as transitions of electrons from one energy state to another, references to unobservable entities may be required to describe the causal factors responsible for the production of specific types of data or data trends. Phenomena thus can be specified in a variety of increasingly accurate manners, and this is one function of models.

Before turning to the role of models in more detail, consider two cases in which the data-phenomena distinction has been involved in considerable controversy. Debate concerning the teaching of evolution in California public schools resulted in a 1989 decision not to allow textbooks to refer to evolution as a "fact". Leaving aside religious motivations, what is clear is that evolution is a phenomenon for which a vast amount of data provides evidence and with respect to which explanatory theories are brought to bear. Theories of evolution are intended to provide an explanatory setting for appropriately modelled phenomena of evolution; they are not concerned with the far more specific details of individual fossils and other data. The textbook controversy thus could have been resolved more appropriately if the distinction between facts about data and facts about phenomena had been understood.

In another celebrated 1989 case, the alleged phenomenon of "cold fusion" was found to be nonexistent in spite of widely publicized evidence. Although Pons and Fleishman claimed to have produced the phenomenon of nuclear fusion at room temperature, their claim was subsequently rejected due to the assessment of their data as idiosyncratic artifacts of experimental equipment. Some of this data continued to be of interest, but by the end of 1989 efforts to give theoretical explanations for the phenomenon of cold fusion had been judged to be premature.

Returning to the domain of solid state chemistry, the transition from data to phenomena often takes place in stages, although not always in the same sequence. For example, the exploration of a new experimental domain usually results in data for variables judged to be of interest. Based upon the state of knowledge in the field, the production of this data is attributed to molecular or atomic phenomena. If possible, noticeable trends or patterns in the data are summarized in phenomenological laws. Structural or interactive mechanisms are proposed as possible causal scenarios. Finally, these mechanisms are modelled in such a way as to be amenable to theoretical explanation by means of approximate application of the Schroedinger equation.

As this process gradually unfolds, there naturally will be speculations about the ultimate outcome. Allegiances to particular modes of modelling or approximation techniques can be expected to color these prognostications. Furthermore, the superficial impression of an inevitable and tidy progression toward explanatory unity often turns out to be more semblance than reality. Distinct groups of scientists are found clustered within distinct stages in the process. Rarely will individuals take part in more than one stage. In part this can be attributed to institutional factors such as industrial or academic employment. In addition, however, disagreement about the value of foundational explanation is to be expected in terms of David Bantz's distinction between the "chemists' picture" and the "physicists' picture" of atomic and molecular structure (Bantz 1980, p. 305).

For example, John Slater is a clear advocate of the physicist's goal of explanatory unity; Nevill Mott, at least during some stages of his long career, gave priority to the "chemists' picture" of the causal structure of phenomena. The two pictures take their distinctive hue from divergent intuitions about which practice contributes more to scientific understanding. Since models link the two pictures, they are judged by two criteria. They thus can be accepted or rejected for different reasons by different individuals. The topic of transition metal oxides provides rich examples of these two ways in which models vie.

4. Models of Transition Metal Oxides

Research in transition metal oxides thoroughly exemplifies the central role of models in solid state physics and chemistry. In particular, the anomalous electrical and

magnetic properties of these materials generated a long series of competing models beginning in the mid-1930's. I will briefly sketch two attempts to model these phenomena, both of which were rejected by 1964. The thermally activated hopping model was designed for incorporation under the Heitler-London mode of explanation by means of localized electrons. Slater's early band theory approach, on the other hand, relied upon the itinerant electron model originally applied to metals by Bloch, Bethe, Peierls and Wilson.

During the 1930's, practical applications of semiconducting transition metal oxides stimulated interest among industrial Dutch scientists such as J. H. de Boer and E. J. W. Verwey at the N. V. Gloeilampenfabrieken in Eindhoven (Schopman 1983 and 1988). In 1937 they called the attention of the international solid state community to the anomalous insulating ground state of nickel oxide (de Boer and Verwey 1937). The occasion was a conference on "The Conduction of Electricity in Solids" organized by Nevill Mott at the University of Bristol where he had become Professor of Theoretical Physics in 1933. De Boer and Verwey pointed out that according to the existing band theory of semiconductors as presented by Wilson in 1931, the incomplete 3d band in nickel oxide meant that it should be a conductor instead of the extremely high resistance insulator it actually is. Their discussion of this anomaly became the incentive for what gradually became articulated as the thermally activated hopping model.

De Boer and Verwey pointed out that, as is the case for CoO and MnO, NiO has the face-centered cubic or rock salt lattice structure of NaCl with doubly charged nickel cations and oxygen anions in alternate positions. Difficult to produce in a pure state, the addition of small amounts of excess oxygen transforms the greenish NiO into a black, slightly nonstoichiometric version. De Boer and Verwey argued that since pure NiO is relatively unstable, the excess oxygen atoms fill some of the empty cation lattice positions rather than being interstitially located. Electrostatic calculations implied that near a vacant lattice point two triply charged nickel ions will form (rather than singly charged oxygen anions) to electrically neutralize the charge deficit. Electric conduction then would require the passage of electrons from one cation to another. This means that an electron must overcome the potential barrier that threatens to trap it at a cation.

De Boer and Verwey concluded that while "the existence of semi-conductors or insulators with partially filled energy zones, could not, indeed, be properly understood from the viewpoint of the present theory of electronic states for metals", their own analysis indicated that the nonconducting state was to be expected "if only the potential barriers are sufficiently high to reduce the frequency of interchange below a certain limit ..." (de Boer and Verwey 1937, p. 66). They thus attributed their high resistance data to specific causal phenomena. In keeping with the practical motivations of their employer, they also investigated the decreased resistance resulting when impurities such as lithium are added to NiO samples. While expanding their account to include what they called the "controlled valency" in these cases, they found that the temperature dependency of resistance followed the exponential phenomenological law typical for semiconductors (Verwey 1951 and Verwey et al 1950).

Meanwhile, Mott had issued something of a manifesto in the form of a challenge to band theory. Due to World War II, he had not immediately been able to devote full attention to the NiO anomaly. In his 1940 book with Gurney, he simply mentioned it in passing as an unresolved theoretical problem (Mott and Gurney 1940, p. 167). Frederick Seitz made a similar comment in his famous 1940 text *The Modern Theory of Solids* (Seitz 1940, p. 468). In 1949, however, Mott published an influential paper in which he argued that nickel oxide is a conductor only when the nickel ions are sufficiently close together to allow some electrons to screen others from the positive attraction to the nu-

cleus; when this happens the screened electrons are not bound to the nucleus and can more readily take up the motion that constitutes an electric current. At electron densities below a certain critical amount, however, the atoms of the crystal are too far apart for this electron screening to take place and the crystal becomes an insulator with bound electrons. Mott supported this interpretation by noting that some semiconductors become metallic conductors when their density is sufficiently increased by the addition of either an impurity or one of the components of the semiconducting compound.

Secondly, Mott also argued that NiO is an example of a substance that cannot be modelled by means of itinerant electrons, and thus cannot be addressed by band theory. Furthermore, London-Heitler approximations, with their reliance upon localized electron models, should break down at some critical pressure when the interatomic distance becomes too small to prevent electron hopping.

Over the next decade, Mott gradually clarified his views on the appropriate scopes for band-theoretic and London-Heitler approximations (Mott 1951, 1952, 1956, and 1958). For band configurations consisting of a combination of entirely full or empty bands, Mott held that both approaches approximate the same exact wave function and correctly predict an insulating ground state. For partially filled bands, however, he claimed that each of the two approximations only applies to certain materials: the London-Heitler method to nonconductors such as NiO, and the band approach to metals.

In 1956 Mott emphasized that his analysis implied that a reduction in the interatomic distance should result in a sharp transition to a conducting state. Furthermore, he claimed that this prediction "is quite different from that of the Bloch-Wilson theory" according to which the transition should be gradual (Mott 1956, p. 1356). His general argument for the discontinuity of these "Mott transitions" was that an ionized electron would be attracted to the accompanying positive hole unless a large number of free carriers are available to shield it. Mott became increasingly fascinated by this controversial interpretation. Indeed, his subsequent assessment of competing models hinged to an important degree upon how much light they shed on Mott transition phenomena.

Meanwhile, during the 1950's experimentalists explored the electrical phenomenology of transition metal oxides in increasing detail. In an effort to determine accurate band structures, F. J. Morin carried out an important series of investigations of transport phenomena at the Bell Laboratories. He used Seebeck effect data to conclude that electron mobility in sintered NiO samples doped with lithium is very low but increases exponentially with temperature (Morin 1958). This became the basis for a widespread conclusion that conduction in these samples is primarily driven by thermal activation of mobility rather than carrier density.

Morin's work contributed to the development of the hopping model due to a study of lithium doped NiO by Heikes and Johnston at the Westinghouse Research Laboratories. Noting that Verwey's initial description of positive holes trapped at lithium sites implied that the activation energy should gradually vanish with increasing lithium percentage, they used the fact that this does not happen to argue that the mobility is the thermally activated factor. They then treated conduction as a diffusion problem and used the Einstein relation to derive Morin's phenomenological law linking mobility to temperature (Heikes and Johnston 1957). Their colleague at Westinghouse, C. Zener, took the occasion of the 1958 International Conference on Semiconductors to declare the limitations of band theory (Zener 1959, p. 27):

Now the term 'semiconductor' has in recent years acquired a connotation
which is associated with the conceptual paraphernalia of band width, band gap,

effective mass, &c. The Westinghouse group has conclusively demonstrated that these conceptual paraphernalia are inappropriate when applied to these transition-metal oxides.

By 1958, then, a specific causal scenario had been established as an alternative to the model relied upon by band theory during the 1930's. According to the thermally activated hopping mechanism, 3d electrons were said to be localized due to Landau trapping, and the increase in conductivity with temperature was attributed to increased mobility as the electrons randomly hop from one site to another.

The final stage we should expect in the development of this approach is a more mathematical representation, a model in the full sense, such that the phenomena construed as thermally activated hopping can be explained by London-Heitler approximation techniques. In 1960 this was indeed carried out by Jiro Yamashita and Tatumi Kurosawa at the Institute for Solid State Physics in Tokyo (Yamashita and Kurosawa 1960). By appropriately formalizing the hopping mechanism as a Heitler-London Hamiltonian, they carried out a series of approximations to arrive at the exponential dependency of mobility on temperature. Their reliance upon the thermally activated hopping model apparently had successfully linked descriptive phenomenological law to explanatory theory.

Nevertheless, the value of this accomplishment soon was seriously eroded by new experimental developments. More accurate measurements of mobility using single crystals rather than sintered samples revealed that mobility does not increase exponentially with temperature and that Hall mobility actually is less than the drift mobility (Ksendzov et al 1963 and Zhuze and Shelykh 1963). These results were in direct contradiction to the central picture of the hopping model. Mott's 1949 claim that the Heitler-London approach was the only possible explanatory route to transition metal oxide phenomena thus was generally rejected between 1963 and 1967 (Adler 1968, pp. 67-72). Furthermore, we find that in this particular case, the model that made possible the explanatory application of Heitler-London theory was rejected primarily because of its failure to represent important phenomena.

Attention thus shifted to surviving rival models. Prominent among these were various revisions of the itinerant electron model at the heart of band theory. Following the 1951 discovery that NiO is antiferromagnetic, Slater had proposed that band theory would have to be extended to take into account electron correlations. At that time he explained how the antiferromagnetic state of NiO could be expected to have an insulating ground state due to an appropriate band splitting. His suggestion was belittled by Mott since it did not account for the nonconducting nature of NiO above the Neel temperature at which it becomes paramagnetic.

Nevertheless, at the same 1958 conference at which Zener proclaimed the death knell for transition metal oxide band theory, Slater persevered and patiently enumerated the idealized mechanisms incorporated into the model relied upon by band theory. In particular, he pointed out that band theory methods had always disregarded correlations among electrons outside closed shells, and he argued that these would have to be included to account for anomalies (Slater 1959, p. 23).

The first unsuccessful attempts to incorporate correlations were carried out by 1963 (Yamashita 1963 and Switendick 1963). For example, only by including p-d mixing, exchange energy and crystal field effects could Switendick use a Hartree-Fock calculation to arrive at an insulating ground state for NiO. Nevertheless, his result erroneously implied ferromagnetism. For Slater this failure meant that a more accurate model would

have to be constructed for the antiferromagnetic-paramagnetic transition; Slater's primary motivation for NiO model selection thus was the need to explain anomalous insulating ground state phenomena. This stands in sharp contrast to the more piecemeal approach to transport phenomena that guided the promotion and demise of the hopping model.

The year 1963 thus marked a significant milestone in transition metal oxide research. New experimental results for transport phenomena brought about the rejection of the thermally activated hopping model. The new data was not compatible with the hopping mechanism that had been modelled and tentatively explained under the Heitler-London approach. On the other hand, Slater and his group at MIT had never taken this "chemists' picture" very seriously; approaching the problem with a predominantly "physicists' picture" emphasis on foundational explanation, their inclination when confronted by new problems was to return to the essential insight of the Hartree-Fock technique and introduce inter-electronic correlation factors. The failure of Switendick's efforts in 1963 thus did not bring this project to a halt. Instead, Slater called for a more general model of magnetic phenomena so as to include the localized magnetic moments of the transition metal oxides as particular cases.

Furthermore, 1963 was also the year in which Hubbard published the first in a series of papers in which he developed a rival narrow 3d band model (Hubbard 1963). The divergent reactions of Mott and Slater illustrate their contrasting evaluative criteria for models. Mott was enthusiastic about Hubbard's work and immediately began applying it in an effort to come to a better understanding of Mott transition phenomena. Slater, on the other hand, was indifferent and wrote in 1967 that:

> ... the direction which I believe is most important, in the solid-state and molecular theory of the next few years, is an extension of the fundamental approach directly from first principles, rather than a proliferation of semiempirical methods (Slater 1967, p. 94).

5. Conclusion

The contrast between Mott and Slater indicates a clear divergence between two evaluative criteria for models of solid state phenomena. This is to be expected in view of the dual role of models. On the one hand, they make possible the application of theoretical formalism and thus are judged according to their compatibility with operative many-body approximation techniques. Slater steadfastly articulated this standard. On the other hand, models act as the culmination of phenomenological description. Solid state physicists and chemists who concentrate on phenomenology thus will sympathize with molecular chemist and Nobel laureate Robert Mulliken:

> ...chemists love molecules, and get to know them individually, in the same way that politicians love people. But what about physicists ? My impression is that they are more concerned with fields of force and waves than with the individual personalities of molecules or of matter, except perhaps in the case of high-energy particles (Mulliken 1968, p. 54).

Similarly, as Mott put it concerning the limited range of one of his mechanisms (Mott 1984, p. 922): "I can hardly doubt that some of these concepts may be falsified over again, but I hope they will suggest worthwhile experiments. That is, after all, what theories are for."

A salient philosophical lesson to be learned here is to eschew declarations about "the" aim of science and to realize that models vie on multiple fronts. This recogni-

tion can then become the basis for an exploration of how these fronts materialize and how they are located within specific academic and industrial contexts.

References

Adler, D. (1968), "Insulating and Metallic States in Transition Metal Oxides", *Solid State Physics* 21: 1-113.

Bantz, D.A. (1980), "The Structure of Discovery: Evolution of Structural Accounts of Chemical Bonding", in T. Nickles (ed.), *Scientific Discovery: Case Studies.* Dordrecht: D. Reidel Publishing Company, pp. 291-329.

Bierlein, J.A. (1955), "A Phenomenological Theory of Soret Diffusion", *Journal of Chemical Physics* 23: 10-14.

Bogen, J. and Woodward, J. (1988), "Saving the Phenomena", *The Philosophical Review* 97: 303-352.

Cartwright, N. (1983), *How the Laws of Physics Lie.* New York: Oxford University Press.

De Boer, J.H. and Verwey, E.J.W. (1937), "Semi-Conductors with Partially and with Completely Filled 3d-Lattice Bands", *Proceedings of the Physical Society* 49 (extra part): 59-71.

Franklin, A. (1987), "Experiment and the Development of the Theory of Weak Interactions: Fermi's Theory", in A. Fine and P. Machamer (eds.), *PSA 1986* Proceedings, vol. 2. East Lansing: Philosophy of Science Association, pp. 163-179.

Galison, P. (1987), *How Experiments End.* Chicago: University of Chicago Press.

_ _ _ _ _ _. (1989), "Multiple Constraints, Simultaneous Solutions", in A. Fine and J. Leplin (eds.), *PSA 1988 Proceedings*, vol. 2. East Lansing: Philosophy of Science Association, pp. 157-163.

Hacking, I. (1983), *Representing and Intervening.* Cambridge: Cambridge University Press.

Heikes, R.R. and Johnston, W.D. (1957), "Mechanism of Conduction in Li-Substituted Transition Metal Oxides", *Journal of Chemical Physics* 26: 582-587.

Heitler, W. (1967), "Quantum Chemistry: The Early Period", *International Journal of Quantum Chemistry* 1: 13-36.

Hubbard, J. (1963), "Electron Correlations in Narrow Energy Bands", *Proceedings of the Royal Society of London* A276: 238-257.

Ksendzov, Ya.M., Ansel'm, L.N., Vasil'eva, L.L., and Latysheva, V.M. (1963), "Investigation of the Carrier Mobility in NiO with Li Impurity", *Soviet Physics - Solid State* 5: 1116-1123.

Laymon, R.(1989), "Cartwright and the Lying Laws of Physics", *Journal of Philosophy* 86: 353-372.

Lowdin, P. O.(1967), "Nature of Quantum Chemistry", *International Journal of Quantum Chemistry* 1: 7-12.

Morin, F. J.(1958), "Oxides of the 3-d Transition Metals", *Bell System Technical Journal* 37: 1047-1084.

Mott, N. (1937), "Discussion of the Paper by De Boer and Verwey", *Proceedings of the Physical Society* 49 (extra part): 72-73.

_ _ _ _ . (1941), "Application of Atomic Theory to Solids", *Nature* 147: 623-624.

_ _ _ _ . (1949), "The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals", *Proceedings of the Physical Society* 62: 416-422.

_ _ _ _ . (1951), "Semi-conductors", in H.K. Henisch (ed.), *Semi-Conducting Materials*. London: Butterworths Scientific Publications, pp. 1-7.

_ _ _ _ . (1952), "Recent Advances in the Electron Theory of Metals", *Progress in Metal Physics* 3: 76-114.

_ _ _ _ . (1956), "On the Transition to Metallic Conduction in Semiconductors", *Canadian Journal of Physics* 34: 1356-1368.

_ _ _ _ . (1958), "The Transition from the Metallic to the Non-Metallic State", *Del Nuovo Cimento* 7 (supplement): 312-328.

_ _ _ _ . (1984), "Metals, non-metals and metal-non-metal transitions: some recollections", *Reports on Progress in Physics* 47: 909-923.

Mott, N. F. and Gurney, R. W. (1948), *Electronic Processes in Ionic Crystals*. 2nd ed. Oxford: Oxford University Press.

Mulliken, R. S. (1968), "Spectroscopy, Quantum Chemistry and Molecular Physics", *Physics Today* 52: 52-57.

Pickering, A. (1984), "Against Putting the Phenomena First: The Discovery of the Weak Neutral Current", *Studies in History and Philosophy of Science* 15: 85-114.

_ _ _ _ _ _ _. (1987), "Against Correspondence: A Constructivist View of Experiment and the Real", in A. Fine and P. Machamer (eds.), *PSA 1986 Proceedings*, vol. 2. East Lansing: Philosophy of Science Association, pp. 196-206.

Schopman, J. (1983), "The Philips' Contribution to Theory and Application of Semi-conducting Oxides (1935-1950)", *Janus* 70: 129-145.

————(1988), "Industrious Science: Semiconductor Research at the N.V. Philips' Gloeilampenfabrieken, 1930-1957", *Historical Studies in the Physical Sciences* 19: 137-172.

Seitz, F. (1940), *The Modern Theory of Solids*. New York: McGraw-Hill.

Slater, J. C. (1959), "Band Theory", *Journal of the Physics and Chemistry of Solids* 8: 21-25.

_____ . (1967), "The Current State of Solid-State and Molecular Theory", *International Journal of Quantum Chemistry* 1: 37-102.

_____ . (1968), "Quantum Physics in America Between the Wars", *Physics Today* 21(1): 43-51.

Switendick, A.C. (1963), "Energy Bands in Nickel Oxide by the Augmented Plane-Wave Method" (abstract), *Bulletin of the American Physical Society* 8: 221.

Verwey, E.J.W. (1951), "Oxidic Semi-conductors", in H.K. Henisch (ed.), *SemiConducting Materials*. London: Butterworths Scientific Publications, pp. 151-161.

Verwey, E.J.W., Haaijman, P.W., Romeijn, F.C. and van Oosterhout, G.W. (1950), "Controlled-Valency Semiconductors", *Philips Research Reports* 5: 173-187.

Woodward J. (1989), "Data and Phenomena", *Synthese* 79: 393-472.

Yamashito, J. (1963), "Electronic Structure of TiO and NiO", *Journal of the Physical Society of Japan* 18: 1010-1016.

Yamashito, J. and Kurosawa, T. (1960), "Heitler-London Approach to Electrical Conductivity and Application to d-Electron Conductions", *Journal of the Physical Society of Japan* 15: 802-821.

Zener, C. (1959), "D-Band and Mixed-Valency Semiconductors", *Journal of the Physics and Chemistry of Solids* 8: 26-28.

Zhuze, V. P. and Shelykh, A. I. (1963), "Hall Effect in Nickel Oxide", *Soviet Physics Solid State* 5: 1278-1280.