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Eric R. Scerri

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The Electronic Configuration Model, Quantum Mechanics and Reduction

ERIC R. SCERRI

ABSTRACT

The historical development of the electronic configuration model is traced and the status of the model with respect to quantum mechanics is examined. The successes and problems raised by the model are explored, particularly in chemical *ab initio* calculations. The relevance of these issues to whether chemistry has been reduced to quantum mechanics is discussed, as are some general notions on reduction.

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-

I INTRODUCTION

This paper deals with some questions in the foundations of chemistry. The atomic orbital (or electronic configuration) model is examined, with regards to both its origins and current usage. I explore the question of whether the commonly-used electronic configuration of atoms have any basis in quantum mechanics as is often claimed particularly in chemical education.

I restrict my attention to non-relativistic pioneer quantum mechanics of 1925–6, and even further to the time independent formulation. Numerous other developments have taken place in quantum theory, such as Dirac's relativistic treatment of the hydrogen atom (Dirac [1928]) and various modern quantum field theories have been constructed (Redhead [1986]). Also, much work has been done in the philosophy of quantum theory such as the question of E.P.R. correlations (Bell [1966]). However, it seems fair to say that no fundamental change has occurred in quantum mechanics since the pioneer version was established. The version of quantum mechanics used on a day-to-day basis by most chemists and physicists remains as the 1925–6 version (Heisenberg [1925], Schrodinger [1926]).

First I consider the origin of tables of electronic configuration which are learned in school chemistry and which appear in all chemistry texts. The aim is

to see if these tables can be derived from quantum theory as is often claimed or implied. Electronic configurations of atoms form the basis for the teaching of chemistry at all levels, and serve to shape the thoughts of even professional chemists.

As Harré [1961] has said concerning models:

they carry the picture with which everyone, schoolboy, student, engineer and research worker, operates in dealing with problems in his field. You may deny that you have a model and be as positivistic as you like, but while the standard expressions continue to be used you cannot but have a picture.

In chemical education, the main motivation for basing chemistry on electronic configurations seems to be that if one knows the number of outer shell electrons in any particular atom, one can predict its chemical properties (Cotton and Wilkinson [1966], Kotz and Purcell [1987]).

2 HISTORICAL

One of the first attempts to explain chemical periodicity in terms of electronic structure was by Niels Bohr [1923]. His method called the 'aufbau principle' consists in building-up successive atoms by the addition of an extra electron to the previous atom. Bohr developed his account of the periodic table according to two quantum numbers, n the main quantum number and k the azimuthal quantum number. These numbers emerge from the quantum conditions and serve to identify the stationary states of the system, that is states which do not vary with time. Electrons in these stationary states do not radiate energy unless they undergo a transition between stationary states. The introduction of stationary states to atomic physics was Bohr's main contribution to the quantum theory of atoms. The problem in classical physics had been to explain why the orbiting electrons did not lose energy and spiral into the nucleus (Jammer [1966]). Bohr postulated that electrons exist in stationary, non-radiating states and only emit radiation on undergoing a transition between stationary states (Bohr [1913]) (Table 1).

According to this scheme an atom of sulphur, for example, with sixteen electrons, would have an electronic configuration of 2, 4, 4, 6 (Bohr [1923]). The main feature of the building-up procedure was Bohr's assumption that the stationary states would also exist in the next atom, obtained by the addition of a further electron. He also assumed that the number of stationary states would remain unchanged apart from any additional states of the newly introduced electron. In other words the assumption was one of the existence of sharp stationary states, and their retention on adding both an electron and a proton to an atom. To quote Bohr:

The demand for the presence of sharp, stable stationary states can be referred to in the language of quantum theory as a general principle of the existence and permanence of quantum numbers.

TABLE 1. Assignment of electrons to shells according to Bohr's scheme.

n	k	Maximum number of electrons
1	1	2
2	1	4
2	2	4
3	1	6
3	2	6
3	3	6
.	.	.
.	.	.

It should be added that the stationary states in the newly obtained atom are not identical, since the accompanying addition of a proton causes a contraction in the size of the electron orbits.

At the basis of the building up procedure used by Bohr there lies the adiabatic principle introduced by Ehrenfest [1917].

If a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions.

Elsewhere Ehrenfest states:

Suppose that for some class of motions we for the first time, introduce the quanta. In some cases the hypothesis fixes completely which special motions are to be considered as allowed. This occurs if the new class of motions are derived by means of an adiabatic transformation from some class of motions already known (Ehrenfest [1917]).

This adiabatic principle was one of the corner-stones of the old quantum theory. It allowed one to find the quantum conditions when an adiabatic change was imposed on a system. It was used successfully to account for the Stark and Zeeman effects in the spectrum of atomic hydrogen, resulting from the application of an electric and magnetic field respectively (Schwartzchild [1916]; Epstein [1916]).

There are however some stringent restrictions on the applicability of the adiabatic principle (Mehra and Rechenberg [1982]). Ehrenfest himself [1917] showed that it was applicable to simply periodic systems. These are systems having two or more frequencies which are rational fractions of each other. In such systems the motion will necessarily repeat itself after a fixed interval of time. Burgers [1917], a student of Ehrenfest, showed that it was also applicable

to multiply periodic systems. In these more general systems of motion the various frequencies are not rational fractions of each other, and so the motion does not necessarily repeat itself (Goldstein [1980]). The hydrogen atom provides an example of a multiply periodic system, with two degrees of freedom being the orbital frequency of the electron, and the precession of the orbital frequency.

An even more general class of systems is termed aperiodic, and as far as we know the adiabatic principle does not apply here. At least nobody has found a proof of its applicability to this day. Unfortunately for the field of atomic physics all atoms larger than that of hydrogen constitute aperiodic systems for which the adiabatic principle does not apply. In the helium atom, for example, the motion of each of the two orbiting electrons varies due to the varying interaction with the other electron as their distance apart changes, in terms of the early Bohr theory. We may no longer speak of a constant period for either of the electrons. Bohr was well aware of this limitation of the adiabatic principle but he continued to use it even for many electron atoms, in the hope that it might still remain valid for these aperiodic systems. He repeatedly acknowledged this point in his writings:

For the purposes of fixing the stationary states we have up to this point only considered simply or multiply periodic systems. However the general solution of the equations frequently yield motions of a more complicated character. In such a case the considerations previously discussed are not consistent with the existence and stability of stationary states whose energy is fixed with the same exactness as in multiply periodic systems. But now in order to give an account of the properties of the elements, we are forced to assume that the atoms, in the absence of external forces at any rate always possess sharp stationary states, although the general solution of the equations of motion for the atoms with several electrons exhibits no simple periodic properties of the type mentioned (Bohr [1923]).

Returning to the historical sequence of events, the hypothesis of the permanence of quantum numbers came under attack from the spectroscopic analysis of the splitting of the lines under the influence of a magnetic field (Lande [1923]). An atomic core consisting of the nucleus and inner shell electrons, showed a total of N spectroscopic terms in a magnetic field. If an additional electron were added, having an azimuthal quantum number k , the new composite system would be expected to show $N(2k-1)$ terms since the additional electron was associated with $2k-1$ terms. However, experiments revealed more terms. In general the terms split into two types, one consisting of $(N+1)(2k-1)$ components and the second consisting of $(N-1)(2k-1)$ components, giving a total number of $2N(2k-1)$ components.

This represents a violation of the number of quantum states, since a two-fold increase in terms of the atomic core seems to occur on the introduction of an additional electron. Bohr's response was to maintain adherence to the

permanence of quantum numbers even in the face of this evidence. He merely alluded to a mystical device which he called a non-mechanical constraint or 'Zwang' to save the quantum numbers (Hendry [1984]).

Bohr's account of the periodic table also came under attack from chemical evidence. The element sulphur, for example, was attributed an electronic configuration of 2, 4, 4, 6 as noted previously. This grouping of electrons suggested that 6 electrons were more loosely bound than the others and successfully accounted for the formation of compounds such as sulphur hexafluoride SF₆. However, this element is also capable of forming a tetrachloride or SCl₄, and a dichloride SCl₂ (Purcell and Kotz [1977]). The formation of these compounds suggests that two or four electrons may be more loosely bound than the remaining electrons, but this notion cannot be accommodated by the configuration given by Bohr.

The next major advance in tables of electronic configurations was provided by the little known English physicist, Stoner [1924]. His approach was based on using not merely two quantum numbers, but also the recently introduced third quantum number of Sommerfeld. The third or inner quantum number *j* refers to the precession of the orbital motion in the presence of a magnetic field. The occurrence of this third quantum number suggested additional stationary states in the atom, and yet Bohr did not extend his electronic configuration scheme accordingly. The reason for this is not clear, but perhaps Bohr was becoming increasingly concerned with the question of the existence of stationary states for individual electrons in many electron atoms. Stoner, undaunted by these theoretical problems, suggested that the number of electrons in each completed level should equal twice the inner quantum number of that particular shell. This produced the scheme for ascribing electrons to shells (Table 2).

TABLE 2. Stoner's scheme for assignment of electronic configurations.

<i>n</i>	<i>k</i>	<i>j</i>	Maximum number of electrons
1	1	1	2
2	1	1	2
2	2	1	2
2	2	2	4
3	1	1	2
3	2	1	2
3	2	2	4
.	.	.	.

According to the Stoner scheme the electronic configuration for the element sulphur, for example, is 2, 2, 2, 4, 2, 2, 2. This configuration could account successfully for the various valency states shown by the element, that is 2, 4, 6 as mentioned before. However, this new scheme did nothing to resolve the problem of the violation of quantum numbers as seen in the splitting of spectral lines in a magnetic field.

In 1923 Bohr wrote to Pauli asking him to try to bring order to the increasingly complicated situation in atomic physics which included the occurrence of half quantum numbers, the problems of the anomalous Zeeman effect and the doublet riddle (the origin of doublets in the X-ray and optical spectra of alkali atoms) (Hendry [1984]). Bohr specifically asked Pauli to attempt to save the quantum numbers. The latter soon responded with two papers which did indeed seem to restore order to atomic physics. Pauli's first main contribution was to challenge the view held at the time, that the core of an atom possesses an angular momentum. This theory had been proposed by Landé in order to explain the origin of the complex structure of atomic spectra. The basic assumption consisted in the interaction of the angular momentum due to the outermost electrons of the atom with that of the inner electrons, or atomic core (Landé [1923]). Pauli began by assuming that the core did indeed have an angular momentum, due to the contribution from the innermost or K shell. He then went on to examine the relativistic consequences of this assumption and was able to show that it was false (Pauli [1925a, b]). The classical expression for the ratio of the magnetic moment M , to the angular momentum J of the innermost shell of the atom is

$$M/J = e/2m_e c$$

where e is the electronic charge, m_e the mass of the electron and c the velocity of light. Pauli's relativistic calculation of this ratio yielded

$$M/J = \gamma e/2m_e c$$

where $\gamma = [1 - \alpha(Z-1)]^{1/2}$, $\alpha = e^2/hc$ is the fine structure constant, and Z is the nuclear charge.

The element barium, to take an example, has a value of $\gamma = .924$ which should result in an easily detectable variation in the ratio M/J , as compared with an element with low nuclear charge. This charge dependence of the ratio had not been observed, and Pauli took this to mean that the initial assumption of an angular momentum for the K shell was in error. He concluded that closed electron shells or the core of an atom contributes nothing to the magnetic moment of an atom. He suggested that the spectral lines and their shifts in the presence of magnetic fields were due entirely to the presence of outer electrons. He went on to suggest the assignment of a fourth quantum number m , to each electron. This fourth number is due in Pauli's words to,

TABLE 3. Allocation of electron shells based on Pauli's scheme. (Modern labels for the quantum numbers have been used instead of *k*'s and *j*'s. This does not alter any of the arguments presented here.)

<i>n</i>	<i>l</i>	<i>m_l</i>	<i>m_s</i>	Maximum number of electrons
1	0	0	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
2	0	0	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
2	1	+1	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
2	1	0	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
2	1	-1	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
3	0	0	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
3	1	+1	$\left\{ \begin{array}{c} +1/2 \\ -1/2 \end{array} \right\}$	2
⋮	⋮	⋮	⋮	⋮

a classically non-describable duplicity in the quantum theoretical properties of the series electron (Pauli [1925a]).

This is the property we now call spin angular momentum. Pauli found that he could obtain Stoner's classification of electronic configurations from the following simple assumption which constitutes the famous exclusion principle in its original form.

It should be forbidden for more than one electron with the same value of the main quantum number *n* to have the same value for the other three quantum numbers *k*, *j* and *m* (Pauli [1925a]).

This is often stated as, 'no two electrons can have the same set of four quantum numbers' (Table 3).

Pauli justified the identification of four quantum numbers with each electron with the following apparently clever argument. He supposed that if a strong magnetic field is applied, the electrons are decoupled and so do not interact, and can be said to be in individual stationary states. Of course, the periodic table arrangement must also apply in the absence of a magnetic field.

In order to maintain the validity of the four quantum numbers for each electron even in the absence of a field Pauli appealed to what he called a 'thermodynamic argument'. He proposed to consider an adiabatic transformation in which the strength of the magnetic field is gradually reduced so that even in the absence of the field the characterization of stationary states for individual electrons remains valid. This argument seems to ensure the existence of sharp stationary states for individual electrons, but how does it fare with regards to the experimental evidence showing a violation in the number of quantum states? This problem was mentioned earlier where we saw that a system expected to show $N(2k-1)$ states on the addition of a single electron to the atomic core was in fact transformed into two sets of states numbering

$$(N+1)(2k-1) \text{ and } (N-1)(2k-1) \text{ states, or a total of } 2N(2k-1).$$

According to Pauli the additional electron possesses $2(2k-1)$ states in contrast to the former view of only $(2k-1)$. The two-fold increase in the number of observed states arises from the proposed duplicity of states of the new electron. The number of states of the atomic core remains as N . The arguments appear very persuasive and were received enthusiastically by the atomic physics community. Not surprisingly Bohr was pleased with Pauli's contribution and congratulated him warmly, although in all fairness both men seemed to view this step as a temporary measure. What they and everybody else failed to notice was that Pauli had committed a fallacy concerning the applicability of the adiabatic principle. A many electron atom constitutes an aperiodic system to which the adiabatic principle does not apply as emphasized by Bohr. Pauli merely changed the argument from the addition of an extra electron as in the aufbau principle, to a single atom in which the strength of a magnetic field is gradually diminished. This does not alter the issue, however, since the system remains aperiodic, and so the adiabatic principle does not apply. Perhaps the reason why such theoretical considerations were suspended was that Pauli's new scheme resolved some major problems. Firstly the existence and permanence of the quantum numbers could be retained as Bohr had hoped. Secondly, the long-standing problem of the closing of electron shells in atoms was resolved. The question had been one of how to explain the series of whole numbers 2, 8, 18, 32... which characterizes the lengths of the periods in the periodic system of chemical elements. These numbers corresponding to the maximum number of electrons in each shell were found to be a consequence of Pauli's principle which forbids any two electrons from sharing the same four quantum numbers and the supposition that the fourth quantum number itself can only adopt two possible values (Pauli [1946]). Pauli was later awarded the Nobel prize for these contributions.

3 PRESENT STATUS AND APPLICATIONS

It is now known that the view of electrons in individual well-defined quantum states represents an approximation. The new quantum mechanics formulated in 1926 shows unambiguously that this model is strictly incorrect. The field of chemistry continues to adhere to the model, however. Pauli's scheme and the view that each electron is in a stationary state are the basis of the current approach to chemistry teaching and the electronic account of the periodic table. The fact that Pauli unwittingly contributed to the retention of the orbital model, albeit in modified form, is somewhat paradoxical in view of his frequent criticism of the older Bohr orbits model. For example Pauli writes,

... We must not put the atoms in the shackles of our prejudices (of which the assumption of electron orbits in the sense of ordinary kinematics is an example); on the contrary we must adapt our concepts to experience (Pauli [1924]).

The new quantum mechanics contradicts this independent electron model as it is often called. In Heisenberg's formulation of quantum mechanics the fundamental equation is,

$$d\hat{F}/dt = i[\hat{H}, \hat{F}]/\hbar$$

where $[\hat{H}, \hat{F}]$ denotes $\hat{H}\hat{F} - \hat{F}\hat{H}$, \hat{F} is any operator, \hat{H} is the Hamiltonian operator of the system and \hbar is $h/2\pi$. If the operators \hat{F} and \hat{H} commute, then the right hand side is equal to zero and any observable corresponding to the operator \hat{F} does not vary with time, *i.e.* is a stationary state. Now it can be shown that the quantum numbers corresponding to individual electrons in a many electron atom do not commute with the Hamiltonian (Pilar [1968]). Only the overall angular momentum quantum number J is found to commute with the Hamiltonian. This number is calculated by the coupling together of individual angular momenta of different electrons. Standard quantum mechanics thus shows that giving electrons individual quantum numbers, or putting them into boxes or orbitals is incorrect.

Pauli's original version of the exclusion principle was found lacking precisely because it ascribes stationary states to individual electrons. According to the new quantum mechanics, only the atomic system as a whole possesses stationary states. The original version of the exclusion principle was replaced by the statement that the wavefunction for a system of fermions must be antisymmetrical with respect to the interchange of any two particles (Heisenberg [1925], Dirac [1928]).

There are two possible cases for the wavefunction of a system of identical fundamental particles such as electrons and photons. These are the symmetric and the antisymmetric cases. Experimental evidence shows that for fermions such as electrons and other particles of half integer spin the wavefunction must be anti-symmetric with respect to the interchange of particle labels. This

represents an additional postulate for quantum mechanics. Further, the anti-symmetry requirement can be shown to arise theoretically from relativistic quantum mechanics. On the other hand it can be shown that bosons or spin zero particles require a symmetric wavefunction (Pauli [1946]). Most of the formulations of quantum mechanics introduce the non-individuality of elementary particles right at the start and do not refer at all to individual particles.

Only the so called first quantisation in particular Schrodinger's formulation, starts off heavily on the wrong foot, by assuming an index, label or name to each particle. But this individualisation is immediately wiped out by systematically permuting the labels of all like particles: Any one labelled particle occurs simultaneously in all positions occupied by like particles (Post [1963]).

Although Pauli's principle was rescued by the new quantum theory, the notion of individual quantum numbers for each electron was lost. The concept of electronic configurations cannot be derived from quantum mechanics. It represents an approximation and a book-keeping scheme for finding the number of outer electrons in an atom, but does not necessarily provide information as to the inner electron shells. The limitations of the model are seldom stated. In the words of Post, it represents a 'floating model' which is neither theoretically justifiable nor experimentally verified (Post [1974], Redhead [1980]). In trying to explain the spectra of atoms we are forced to abandon configurations and to consider coupling schemes between the various electrons. Configurations themselves are not directly observable.

In spite of the insecure basis which the orbital model possesses, it has proved fruitful in the field of atomic chemistry and physics. Firstly the use of electronic configurations serve as a basis for the classification of the lines shown by atomic spectra (Condon and Shortley [1935], Slater [1949]).

The first 100 to 400 J levels in all atoms can be classified on the basis of terms arising from assumed electronic configurations for the ground and excited states. These J levels are characterized by the value of the overall angular momentum of the atom. The various J levels arise from the removal of degeneracy from states corresponding to any particular presumed electronic configuration. This process may be thought of as occurring in two stages. First the Coulombic repulsion between electrons produces a number of spectroscopic terms with differing values for the quantum numbers L and S or orbital and spin angular momentum respectively. Secondly the inclusion of coupling between the orbital and spin angular momenta causes further splitting of lines into levels characterized by the overall angular momentum quantum number or J . These J values alone represent spectroscopic observables, while the L and S quantum numbers for the whole atom as well as the quantum numbers for each of the individual electrons are not observed.

A mark of the success of this theory lies in the fact that no low lying superfluous J levels have been found which defy classification according to a plausible electronic configuration for the atom in question. On the other hand, there are sometimes predicted levels which have not yet been observed as in the case of three of the six terms for the s^1p^3 configuration in carbon (Moore [1949]).

There are some rather impressive cases of the resolution of almost complete configurations in atoms known to have very complex spectra. For example 38 of the predicted 41 J levels have been found in the lowest configuration of $[Xe] 4f^3$ (Sugar [1963]), and 101 out of a predicted 107 J levels of the next lowest configuration $[Xe] 4f^2 5d^1$ in the Pr^{+2} ion (Trees [1964]). Very recently 33 out of 34 predicted J levels have been detected in the Mn^{+3} ion with a configuration of $3d^4$ (Tchang-Brillet *et al.* [1986]), and 32 out of a predicted 34 J levels in the Ni^{+6} ion having the same electronic configuration (Van het Hof *et al* [1989]).

However, the taxonomic effectiveness of electronic configurations is not a basis for thinking that quantum mechanics can successfully account even for the restricted field of atomic chemistry. Clearly, molecular quantum chemistry is even less secure due to the additional assumptions which must be made apart from the validity of atomic orbitals.

Moreover the conventional theory of atomic spectra itself is forced to admit the element of configurational mixing in order to account for some of the discrepancies encountered between predictions and the observed ordering and spacing of spectral lines. Configurational mixing simply denies the assumption of a single fixed configuration for an atom. This feature has been known since the original development of the theory of atomic spectra through the work of Ufford and Shortley [1932] and Condon [1929], among others.

One contemporary author has described the situation regarding atomic spectroscopy in the following manner:

Taxonomic classification invariably have been first (and frequently the only until now) constructive influence of quantum theory on a given area in chemistry, and numerical approximations to wavefunctions have been remarkably unproductive compared with the enormous amount of mathematical quantities handled by modern computers (Jorgensen [1986]).

Overall, the effectiveness of electronic configurations in the classification of spectral lines is surprising as expressed by Jorgensen [1971].

Nature plays a masquerade and behaves as if electron configurations most frequently are meaningful. They are taxologically valid. We do not know why.

The second main application of the orbital model lies with *ab initio* calculations in chemistry (Szabo and Ostlund [1982]). The basic problem is to calculate the energy of an atom, for example, from first principles, without recourse to any experimental facts. The procedure consists in solving the time independent Schrodinger for the atom in question, but unfortunately only

hydrogenic systems such as H , He^+ and Li^{+2} which have a single electron possess exact solutions.

In the case of many electron atoms, the Hamiltonian operator includes terms due to inter-electronic repulsions. Nobody has yet discovered any means of solving such equations exactly, and a variety of approximation methods have been devised. In the vast majority of these schemes it is assumed as a zero order approximation, that the atomic wavefunction may be expressed as a product of wavefunctions of independent electrons, or in other words the orbital approximation is used. All efforts are then directed towards accounting for the interaction between electrons which is denied by the zero order theory. The most commonly used Hartree–Fock method consists of an iterative procedure which calculates the average configuration of all the electrons in the atom. The method is described as a self-consistent calculation since the energy of each electron is minimized with respect to every single other electron in the atom (Hartree [1957]). It fails to capture instantaneous changes in configurations, however, and the latter may be modelled by several approaches including configuration interaction (Shavitt [1984]), cluster methods (Sinanoglu [1961]), many body perturbation theory (Wilson [1984]) and several other more recent methods (Wilson [1987]).

Alternative methods are based on the pioneering work of Hylleraas ([1928], [1964]). In these cases orbitals do not form the starting point, not even in zero order. Instead, the troublesome inter-electronic terms appear explicitly in the expression for the atomic wavefunction. However the Hylleraas methods become mathematically very cumbersome as the number of electrons in the atom increases, and they have not been very successfully applied in atoms beyond beryllium, which has only four electrons. Interestingly, one recent survey of *ab initio* calculations on the beryllium atom showed that the Hylleraas method in fact produced the closest agreement with the experimentally determined ground state atomic energy (Froese-Fischer [1977]).

Another problem associated with most orbital based calculations concerns the convergence of the atomic and molecular wavefunction. This is a notoriously difficult problem which has not been solved generally (Klahn and Bingel [1977]). Although it is perfectly legitimate to represent an atomic or molecular wavefunction as an infinite series of terms due to independent electron functions, in practice the series must be truncated in order to carry out a calculation. In many cases the point at which truncation is carried out appears to be arbitrary. Indeed many theoretical chemists pride themselves on the artistry involved in knowing at what point an expansion should be truncated in order to obtain good agreement with experimental data. As some authors have pointed out, a truly *ab initio* calculation should provide an unambiguous and systematic theoretical criterion for truncation, which is independent of comparison with experimental data, as well as an estimate of the expected error for the calculation (Weinhold [1972], Schwartz [1963]).

Furthermore, the reliance on experimental data to check the validity of calculations presents a certain dilemma, since it is precisely in cases where little or no experimental data are available that calculations would be of the greatest benefit.

4 CONCLUSIONS

I conclude that in many *ab initio* calculations the orbital approximation represents the only practical approach, but its proponents might benefit by moderating their claims to success. As an example of a recent exaggerated claim we find.

In the future we expect to find an increasing number of situations in which the theory will be the preferred source of information for aspects of complex chemical systems (Wasserman and Schaefer [1986]).

Since in most cases convergence has not been proved, these authors are merely playing the game of the wise gambler who quits while he is still winning. There is no guarantee that a series which seems to be converging, will not start to diverge after a certain point. Convergence must ideally be proved analytically independently of experimental data. Even if the orbital approach could be shown to be entirely successful in these terms it would still be wrong to conclude that atomic chemistry had been reduced by quantum mechanics since the use of orbitals is strictly denied by this theory.

Similarly the apparent success shown by orbital model as a zero order basis for the classification of spectral lines should not be taken to suggest a reduction of the chemical phenomena to quantum mechanics.

The problems which the orbital approximation raises in chemical education have been discussed elsewhere by the author (Scerri [1989], [1991]). Briefly, chemistry textbooks often fail to stress the approximate nature of atomic orbitals and imply that the solution to all difficult chemical problems ultimately lies in quantum mechanics. There has been an increasing tendency for chemical education to be biased towards theories, particularly quantum mechanics. Textbooks show a growing tendency to begin with the establishment of theoretical concepts such as atomic orbitals. Only recently has a reaction begun to take place, with a call for more qualitatively based courses and texts (Zuckermann [1986]). A careful consideration of the orbital model would therefore have consequences for chemical education and would clarify the status of various approximate theories purporting to be based on quantum mechanics.

The claim that even atomic chemistry has been reduced to quantum mechanics would appear to be highly exaggerated according to the arguments we have presented. To those interested in theory reduction in general this conclusion may not be so surprising. It appears to be increasingly acknow-

ledged that strict theory reduction as envisaged by Nagel [1961] among others is not tenable. Nagel's views have been criticized by many authors, and the overall conclusion seems to be that we may only speak of approximate reduction (Nickles [1973], Sklar [1967], Vollmer [1984]). There are even those who deny that reduction of any form cannot be achieved (Feyerabend [1962], Kuhn [1962]). These views are not shared by the present author and will not be discussed further. The majority of scientists still hold that the special sciences are in some sense reducible to physics. Similarly a number of philosophers are not prepared to abandon the notion of reduction altogether, but try to refine the views of Nagel on the subject. Following our examination of the orbital model, we wish to point out that it represents an even weaker form of reduction than the frequently discussed approximate reductions. For example the reduction of the laws describing ideal gases by classical kinetic theory provides a good example of approximate reduction.

In this model the gas particles are assumed to show no interactions between each other. This model can be realized or at least approached closely in a physical sense, since under conditions of low pressure and high temperatures interaction between particles becomes progressively weaker. Another example consists in the relationship between relativistic and classical mechanics. The relativistic expression for momentum.

$$p = m_0 v / (1 - v^2/c^2)^{1/2}$$

reduces to the classical expression

$$P = m_0 v$$

as the velocity tends to zero. Once again this reduction can be achieved physically by reducing the velocity.

However, in the case of the electronic orbital model there is no way in which the inter-electronic repulsions can be physically reduced. This form of distinction has not been sufficiently emphasized by philosophers. I believe that the nature of the orbital model shows that not all theoretical models can be lumped together as in the work of Achinstein [1968].

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King's College, London

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