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JUST HOW AB INITIO IS AB INITIO QUANTUM CHEMISTRY?[*]

1. INTRODUCTION

Quantum Mechanics has been the most spectacularly successful theory in the history of science. As is often mentioned the accuracy to which the gyromagnetic ratio of the electron can be calculated is a staggering nine decimal places. Quantum Mechanics has revolutionized the study of radiation and matter since its inception just over one hundred years ago. The impact of the theory has been felt in such fields as solid state physics, biochemistry, astrophysics, materials science and electronic engineering, not to mention chemistry, the subject of this conference.

Quantum Mechanics offers the most comprehensive and most successful explanation of many chemical phenomena such as the nature of valency and bonding as well as chemical reactivity. It has also provided a fundamental explanation of the periodic system of the elements that summarizes a vast amount of empirical chemical knowledge. Quantum Mechanics has become increasingly important in the education of chemistry students. The general principles provided by the theory mean that students can now spend less time memorizing chemical facts and more time in actually thinking about chemistry.

I hope that with these opening words I have succeeded in convincing the audience that I do not come before you to deny the power and influence of Quantum Mechanics in the field of chemistry.

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2. THE AIM OF THIS WORK

My project is somewhat different. With the triumph of quantum mechanics there has been an inevitable tendency to exaggerate its success, especially on the part of practicing quantum chemists and physicists. As a philosopher of chemistry I have the luxury of being able to examine the field as an outsider and of asking the kinds of questions which true practitioners might not even contemplate.

Quantum mechanics is part of the reductionist tradition in modern science, and the general claim, often just made implicitly as in any branch of reduction, is that the highest ideal one can aspire to is to derive everything from the theoretical principles. The less experimental data one needs to appeal to, the less one is introducing measured parameters the purer the calculation and the closer it approaches to the ideal of Ockham's razor of being as economical as possible (Hoffmann et al., 1996).

Of course there is no such thing as a completely *ab initio* calculation and if one looks far enough back at the history of any scientific theory one finds that it began with the assumption of at least some experimental data. But it is also fair to say that once the basic principles of a theory have been arrived at, the theorist may 'kick away' the historical-experimental scaffolding. The modern student of quantum mechanics, for example, is not obliged to follow the tortuous route taken by Planck, Einstein, De Broglie, Schrödinger and others. She can go directly to the postulates of quantum mechanics where she will find procedures for doing all kinds of calculations and she can safely ignore the historical heritage of the theory. Indeed many argue, and correctly in my view, that it is actually a hindrance for the practitioner to get too involved in the historical aspects of the theory although it may of course be culturally enriching to do so.

The epitome of the ab initio approach is something like Euclidean geometry where one begins with a number of axioms and one derives everything from this starting point without any recourse whatsoever to empirical data. Needless to say geometry, Euclidean or otherwise, has its origins in the dim distant past when agrarian man needed to think about lines and angles and areas of land. But once the concepts of line, angle and distance had been sufficiently abstracted the agrarian heritage could be completely forgotten.

In a similar way my question today is going to be to ask to what extent the periodic table of the elements can be *explained* strictly from first principles of quantum mechanics without assuming any experimental data whatsoever. I suspect that some physicists and chemists in the audience might well experience some irritation at the almost perverse demands which I will make on what should be derivable from the current theory. If so then I apologize in advance.

By adopting a perspective from the philosophy of science we will cross levels of complexity from the most elementary explanations based on electron shells to frontier ab initio methods. Such a juxtaposition is seldom contemplated in the chemical literature. Textbooks provide elementary explanations that necessarily distort the full details but allow for a more conceptual or qualitative grasp of the main ideas. Meanwhile the research literature focuses on the minute details of particular methods or particular chemical systems and does not typically examine the kind of explanation that is being provided. To give a satisfactory discussion of explanation in the context of the periodic table we need to consider both elementary and supposedly deeper explanations within a common framework.

One of the virtues of philosophy of science is that it can bridge different levels in this way since it primarily seeks the 'big picture' rather than the technical details. In fact supposedly elementary explanations often provide this big picture in a more direct manner but what is also needed is to connect the elementary explanation to the technical details in the deeper theories.

The question of whether or not different levels of explanation for any particular scientific phenomenon are in fact consistent and whether they form a seamless continuum has been the subject of some debate. For example in her first book Nancy Cartwright goes to some lengths to argue that many different explanations can be found for the action of lasers and suggests that these explanations are not necessarily consistent with each other (Cartwright, 1983). In other writings she has expressed some support for the thesis that the various special sciences are dis-unified (Cartwright, 1996).

My own view differs from Cartwright's in that I am of the opinion that the sciences are unified and that explanations given for the same scientific phenomenon at different levels are essentially consistent, although the connection if frequently difficult to elaborate in full

(Scerri, 2000). In this paper I will attempt to draw such connections for the various explanations of the periodic table given at different levels of sophistication.[1]

3. FIRST AN ELEMENTARY APPROACH

Let us start at an elementary level or with a typically 'chemical' view. Suppose we ask an undergraduate chemistry student how quantum mechanics explains the periodic table. If the student has been going to classes and reading her book she will respond that the number of valency or outer-shell electrons determines, broadly speaking, which elements share a common group in the periodic table. The student might possibly also add that the number of outer-shell electrons *causes* elements to behave in a particular manner.

Suppose we get a little more sophisticated about our question. The more advanced student might respond that the periodic table can be explained in terms of the relationship between the quantum numbers which themselves emerge from the solutions to the Schrödinger equation for the hydrogen atom.[2]

This more sophisticated explanation for the periodic system is provided in terms of the relationship between the four quantum numbers that can be assigned to any electron in a many-electron atom. The first quantum number n can adopt any integral value starting with 1. The second quantum number which is given the label ℓ can have any of the following values related to the values of n,

$$\ell = n - 1, \ldots 0$$

In the case when n = 3 for example, ℓ can take the values 2, 1 or 0. The third quantum number labeled m_ℓ can adopt values related to those of the second quantum numbers by the relationship,

$$m_\ell = -\ell, -(\ell + 1), \ldots 0 \ldots (\ell - 1), \ell$$

For example if $\ell = 2$ the possible values of m_ℓ are,

$$-2, -1, 0, +1, +2$$

Finally, the fourth quantum number labeled m_s can only take two possible values, either $+1/2$ or $-1/2$ units of spin angular

momentum. We thus have a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom. These relationships are derived theoretically and do not involve the use of any experimental data.[3]

For example, if the first quantum number is 3 the second quantum number ℓ can take values of 2, 1 or 0. Each of these values of ℓ will generate a number of possible values of m_ℓ and each of these values will be multiplied by a factor of two since the fourth quantum number can adopt values of 1/2 or $-1/2$. As a result there will be a total of $2 \times (3)^2$ or 18 electrons in the third shell. This scheme thus explains *why* there will be a maximum total of 2, 8, 18, 32 etc. electrons in successive shells as one moves further away from the nucleus.

## 4. HOW DOES THIS EXPLAIN THE FORM OF THE PERIODIC TABLE?

But does the fact that the third shell can contain 18 electrons also explain why some of the periods in the periodic system contain eighteen places? Actually not exactly. If electron shells were filled in a strictly sequential manner there would be no problem and the explanation would in fact be complete. But as anyone who has studied high school chemistry is aware, the electron shells do not fill in the expected sequential manner. The configuration of element number 18, or argon is,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$
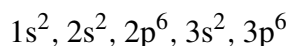
This might lead one to think that the configuration for the subsequent element, number 19, or potassium, would be

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1$$
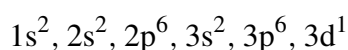
since up to this point the pattern has been to add the new electron to the next available orbital in the sequence of orbitals at increasing distances from the nucleus. However experimental evidence shows quite clearly that the configuration of potassium should be denoted as,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$
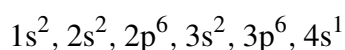
As many textbooks state this fact can be explained from the fact that
the 4s orbital has a lower energy than the 3d orbital. In the case of
element 20 or calcium the new electron also enters the 4s orbital and
for the same reason.

5. TRANSITION METAL CONFIGURATIONS

The interesting part is what happens next. In the case of the next
element, number 21, or scandium, the orbital energies have reversed
so that the 3d orbital has a lower energy, as shown in Figure 1. Text-
books almost invariably claim that since the 4s orbital is already full
there is no choice but to begin to occupy the 3d orbital. This pattern
is supposed to continue across the first transition series of elements,
apart from the elements Cr and Cu where further slight anomalies
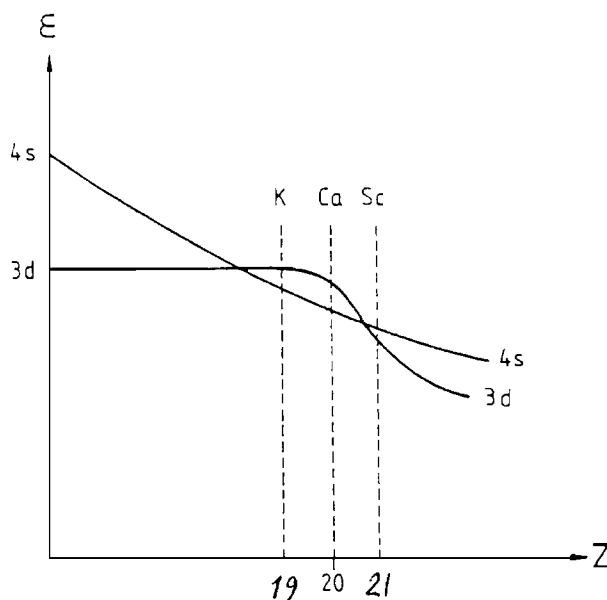are believed to occur.

Figure 1.   Variation of 4s and 3d orbital energies as a function of Z, atomic
number.

In fact this explanation for the configuration of the scandium
atom and most other first transition elements is inconsistent. If the
3d orbital has a lower energy than 4s starting at scandium then if

TABLE I

Table of configurations of first transition series

Sc	Ti	V	Cr	Mn	Fe
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$
	Co	Ni	Cu	Zn	
	$4s^23d^7$	$4s^23d^8$	$4s^23d^9$	$4s^13d^{10}$	

one were really filling the orbitals in order of increasing energy one would expect that all three of the final electrons would enter 3d orbitals. The argument which most textbooks present is incorrect since it should be possible to predict the configuration of an element from a knowledge of the order of its own orbital energies (Scerri, 1989; Vanquickenborne et al., 1994). It is incorrect to consider the configuration of the previous element and assume that this configuration is carried over intact on moving to the next element, especially in cases where orbital energies cross over each other as they do in this case. It should be possible to predict the order of orbital filling for the scandium atom on its own terms. If one tries to do so, however, one predicts a configuration ending in $3d^3$, contrary to the experimental facts.

The full explanation of why the $4s^23d^1$ configuration is adopted in scandium, even though the 3d level has a lower energy, emerges from the peculiarities of the way in which orbital energies are defined in the Hartree–Fock procedure. The details are tedious but have been worked out and I refer anyone who is interested in pursuing this aspect to the literature (Melrose and Scerri, 1996).[4]

6. HOW ARE CONFIGURATIONS DERIVED FROM THE THEORY?

But let me return to the question of whether the periodic table is fully and deductively explained by quantum mechanics. In the usually encountered explanation one assumes that at certain places in the periodic table an unexpected orbital begins to fill as in the case of potassium and calcium where the 4s orbital begins to fill before the 3d shell has been completely filled (Scerri, 1989). This information itself is not derived from first principles. It is justified *post facto* and

TABLE II

Calculated energy levels for two scandium atom configurations

Sc	$4s^2 3d^1$		
	Non-Relativistic	-759.73571776	(atomic units or Hartrees)
	Relativistic	-763.17110138	
	$4s^1 3d^2$		
	Non-Relativistic	-759.66328045	
	Relativistic	-763.09426510	

by some very tricky calculations at that (Melrose and Scerri, 1997; Vanquickenborne et al., 1994).

But if we ignore the conceptual paradox of why 4s fills preferentially even though it has a higher energy than 3d we can just concentrate on calculations aimed at determining the ground state configuration. Suppose we were to use the most widely used method for calculating the energies of atoms and molecules in an ab initio fashion. The Hartree–Fock method[5] can be used to compare the energies of the scandium atom with two alternative configurations,

$$[Ar]4s^2 3d^1 \quad \text{and} \quad [Ar]4s^1 3d^2$$
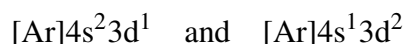
This can be carried out using ordinary non-relativistic quantum mechanics or alternatively by including relativistic effects. The results of using a readily available program on the Internet, created by Froese Fischer[6] one of the leaders in the field of Hartree–Fock calculations, shown in Table II (http://hf5.vuse.vanderbilt.edu/hf.html).[7]

In each case the more negative the calculated value of the energy the more stable the configuration. Clearly the inclusion of relativistic effects serves to reduce the energy from the non-relativistic value. In the case of scandium it appears that both non-relativistic and relativistic *ab initio* calculations correctly compute that the $4s^2$ configuration has the lowest energy in accordance with experimental data. But these calculations, including the ones for subsequent elements must be done on a case-by-case basis. There is not yet a general derivation of the formula which governs the order of filling, sometimes called the $n + \ell$, or Madelung rule, which states that given

TABLE III

Calculated energy levels for two chromium atom configurations

Cr	$4s^1 3d^5$	
	Non-Relativistic	-1043.14175537
	Relativistic	-1049.24406264
	$4s^2 3d^4$	
	Non-Relativistic	-1043.17611655
	Relativistic	-1049.28622286

a choice of filling any two orbitals the order of filling goes according to increasing values of n + ℓ. For example, 4s where n + ℓ = 4, fills before 3d where n + ℓ = 5. But similar calculations do not fare as well in other atoms. Consider the case of the chromium atom for example.

It appears that both non-relativistic and relativistic calculations fail to predict the experimentally observed ground state which is the $4s^1 3d^5$ configuration, as seen in Table III. Of course I do not deny that if one goes far enough in a more elaborate calculation then eventually the correct ground state will be recovered. But in doing so one knows what one is driving at, namely the experimentally observed result. This is not the same as strictly predicting the configuration in the absence of experimental information. In addition, if one goes beyond the Hartree–Fock approximation to something like the configuration interaction approach there is an important sense in which one has gone beyond the picture of a certain number of electrons in a set of orbitals.[8] Rather than just having every electron in every possible orbital in the ground state configuration we now have every electron in every one of thousands or even millions of configurations each of which is expressed in terms of orbitals.

7. COPPER ATOM

Let me consider the case of the copper atom calculated to the same degree of accuracy via the Hartree–Fock method. For this atom the experimentally observed ground state configuration is $4s^1 3d^{10}$.

TABLE IV

Calculated energy levels for two copper atom configurations

Cu	$4s^13d^{10}$	
	Non-Relativistic	-1638.96374169
	Relativistic	-1652.66923668
	$4s^23d^9$	
	Non-Relativistic	-1638.95008061
	Relativistic	-1652.67104670

From Table IV, we see that sometimes a non-relativistic calculation gives the correct result ($4s^13d^{10}$), in terms of which configuration has the lower energy, and yet carrying out the calculation to a greater degree of accuracy by including relativistic effects, gives the wrong prediction. Relativistically one predicts the opposite order of stabilities than what is observed experimentally. Clearly some observed electronic configurations cannot yet be successfully calculated from first principles, at least at this level of approximation. The fact that copper has a $4s^13d^{10}$ configuration rather than $4s^23d^9$ is an experimental fact. Similarly it is from experimental data that the lengths of the periods are known and not from ab initio calculations.

The development of the period from potassium to krypton is not due to the successive filling of 3s, 3p and 3d electrons but due to the filling of 4s, 3d and 4p. It just so happens that both of these sets of orbitals are filled by a total of 18 electrons.

As a consequence the explanation for the form of the periodic system in terms of how the quantum numbers are related is semi-empirical since the order of orbital filling is obtained from experimental data. Consider now the cumulative total number of electrons which are required for the filling successive shells and periods, respectively,

Closing of shells,
Occurs at Z = 2, 10, 28, 60, 110 (cumulative totals)

Closing of periods,
Occurs at Z = 2, 10, 18, 36, 54, etc.

It is the second sequence of Z values which really embodies the periodic system and not the first. For all we know, electron shells may not even exist or may be replaced by some other concept in a future theory. But the fact that chemical repetitions occur at Z = 3, 11 and 19, if we focus on the alkali metals, for example are chemical facts which will never be superceded.

Only if shells filled sequentially, which they do not, would the theoretical relationship between the quantum numbers provide a purely deductive explanation of the periodic system. The fact that the 4s orbital fills in preference to the 3d orbitals is not predicted in general for the transition metals but only rationalized on a case by case basis as we have seen. In some cases the correct configuration cannot even be rationalized, as in the cases of chromium and copper, at least at this level of approximation. Again, I would like to stress that whether or not more elaborate calculations finally succeed in justifying the experimentally observed ground state does not fundamentally alter the overall situation.[9]

To sum-up, we can to some extent recover the order of filling by calculating the ground state configurations of a sequence of atoms but still nobody has deduced the n + ℓ rule from the principles of quantum mechanics. Perhaps this should be a goal for quantum chemists and physicists if they are really to explain the periodic system in terms of electronic configurations of atoms in ab initio fashion.

8. NICKEL ATOM

The case of nickel turns out to be interesting for a different reason. According to nearly every chemistry and physics textbook the configuration of this element is given as

$$4s^2 3d^8$$

However the research literature on atomic calculations (e.g., Bauschlicher et al., 1988) always quotes the configuration of nickel as

$$4s^1 3d^9$$

TABLE V

Quantum mechanical calculations for the nickel atom

Ni	$4s^2 3d^8$	
	Non-Relativistic	-1506.87090774
	Relativistic	-1518.68636410
	$4s^1 3d^9$	
	Non-Relativistic	-1506.82402795
	Relativistic	-1518.62638541

The difference occurs because in more accurate work one considers the average of all the components arising from a particular configuration and not just the lowest possible component of the ground state term. Nickel is somewhat unusual in that although the lowest energy term arises from the $4s^2 3d^8$ configuration it turns out that the average of the energies of all the components arising from this configuration lies higher in energy than the average of all the components arising from the configuration of $4s^1 3d^9$. As a consequence the $4s^2 3d^8$ configuration is regarded as the ground state in research work and it is this average energy which is compared with experimental energies as in Table V. When this comparison is carried out it emerges that the quantum mechanical calculation using either a non-relativistic or a relativistic Hartree–Fock approach gives the wrong ground state.

Of course the calculations can be improved by adding extra terms until this failure is eventually corrected. However, these additional measures are only taken after the facts are known. In addition, the lengths to which theoreticians are forced to go to in order to obtain the correct experimental ordering of terms does not give one too much confidence in the strictly predictive power of quantum mechanical calculations in the context of the periodic table. For example, the very accurate calculations on nickel include the use of basis sets which extend up to 14s, 9p, 5d as well as f orbitals (Raghavachari and Trucks, 1989).[10]

9. CHOICE OF BASIS SET

There is yet another general problem which mars any hope of claiming that electronic configurations can be fully predicted theoretically and that quantum mechanics thus provides a purely deductive explanation of what was previously only obtained from experiments. In most of the configurations we have considered, with the exception of cases mentioned above, it has been possible to use a quantum mechanical method to calculate that this particular configuration does indeed represent the lowest energy possibility. However, in performing such calculations the candidate configurations which are subjected to a variation procedure are themselves obtained from the aufbau principle and other rules of thumb such as Hund's principle or by straightforward appeal to experimental data.

There is a very simple reason for this state of affairs. The quantum mechanical calculations on ground state energies involve the initial selection of a basis set, which in its simplest, or minimal, form is the electronic configuration of the atom in question. Quantum mechanical calculations are not capable of actually generating their own basis sets that must instead be put in 'by hand'. So whereas the correct ground state electronic configurations can in many cases be selected among a number of plausible options, the options themselves are not provided by the theory. I suggest this is another weakness of the present claims to the effect that quantum mechanics explains the periodic system and it is an aspect that might conceivably corrected by future developments.

I will now attempt to take stock of the various senses of the claim that the periodic system is reduced, or fully explained, by quantum mechanics and to extend the scope of this work to more elaborate theoretical approaches.

10. QUALITATIVE EXPLANATION OF PERIODIC TABLE IN TERMS OF ELECTRONS IN SHELLS

The usually given 'explanation' for the period table takes a qualitative form. In broad terms the approximate recurrence of elements after certain regular intervals is explained by the possession of a certain number of outer-shell electrons. This form of explanation

appears to be quantitative to some people because it deals in number of electrons but in fact turns out to be rather qualitative in nature. It cannot be used to predict quantitative data on any particular atom with any degree of accuracy.

Whereas the crude notion of a particular number of electrons in shells or orbitals does not produce very accurate calculations the process can be refined in several ways. The first refinement is perhaps the use of the Hartree method of calculating self-consistent orbitals while at the same time minimizing the energy of the atom.[11] The next refinement lies in making the method consistent with the notion that electrons are indistinguishable. This requirement is met by performing a permutation of all the electrons in the atom so that each electron finds itself simultaneously in all occupied orbitals at once. It is represented mathematically as a determinant that includes all possible permutations within it.

The third refinement is to include any number of excited state configurations for the atom, in a procedure called configuration interaction or the C.I. method. One now has a sum of determinants each of which represents a particular configuration and which is included in the overall atomic wavefunction with a particular weighting determined by a coefficient which is multiplied by the appropriate determinant.

$$\Psi = c_1 D_1 + c_2 D_2 + \ldots$$

The calculation consists in finding the optimum weighting which all the determinants must have in order to minimize the energy of the atom. Having reached this level of abstraction we have really left behind the homely picture of electrons in particular shells. If one still insists on visualization, each electron is now in every orbital of every single configuration that we choose to consider.

Clearly there is still a connection with the elementary homely model but it is also fair to say that the move towards greater abstraction has somewhat invalidated the naïve model. This now raises the question as to whether the elementary model really does have explanatory power. I would argue that it does not. It may have led historically to these more sophisticated approaches but it has been rendered vastly more abstract in the process.

But if we are considering the general question of explanation it is not essential to retain the homely picture that can be grasped by the

general chemist or the beginning student of physical chemistry. We must move on to enquire about how the more abstract approaches actually fare. The short answer is much better but still not in strictly ab initio fashion.

11. NECESSARY AND SUFFICIENT CONDITIONS

But in any case even within the elementary model it emerges that the possession of a particular number of outer-shell electrons is neither a necessary nor a sufficient condition for an element's being in any particular group. It is possible for two elements to possess exactly the same outer electronic configuration and yet not to be in the same group of the periodic system. For example, the inert gas helium has two outer-shell electrons and yet is not usually placed among the alkaline earth elements such as magnesium, calcium or barium, all of which also display two outer-shell electrons.[12] The possession of a particular number of outer-shell electrons is therefore not sufficient grounds for placing it in a particular group.

Conversely, there are cases of elements that do belong in the same group of the periodic table even though they do not have the same outer-shell configuration. In fact this occurrence is rather common in the transition metal series. To take one interesting example,[13] consider the nickel group in which no two elements show the same outer shell configuration!

$$Ni \quad [Ar] \, 4s^2 3d^8$$
$$Pd \quad [Kr] \, 4s^0 3d^{10}$$
$$Pt \quad [Xe] \, 4s^1 3d^9$$
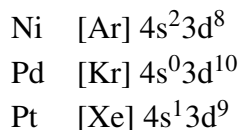
In addition the very notion of a particular number of electrons in a particular shell stands in strict violation of the Pauli Principle, arguably one of the most powerful principles in the whole of science. This states that electrons cannot be distinguished, which implies that we can never really state that a particular number belong in one shell and another number in a different shell, although there is no denying the usefulness of making this approximation. The independent-electron approximation, as it is known, represents one of the central

paradigms in modern chemistry and physics and of course I am not denying its usefulness but am focusing on its ontological status.

But all this talk of electrons in shells and orbitals is just naïve realism. The lesson from quantum mechanics is the need to abandon naïve realism, to abandon picturing waves or particles or picturing spinning electrons.[14] The standard, or Copenhagen, interpretation of quantum mechanics urges us to just do the mathematics and adopt an instrumental approach to the theory. Of course this is hard especially for chemists since most of their work consists in shapes, structures, diagrams, pictures, representations and observable changes. Let us finally consider explanations of the periodic table that do not involve picturing electrons in shells or orbitals.[15]

12.   AB INITIO CALCULATIONS BASED ON WAVEFUNCTIONS

Some of the more abstract ab initio approaches have already been described above. They are the Hartree–Fock method and the configuration interaction approach.

Indeed, such approaches fare much better, and are serious contenders for the claim to a full explanation of the periodic system. In order to illustrate both the power and the pitfalls of the methods I will focus for simplicity on the ab initio calculation of ionization energies of atoms. In this approach the notion of electrons in shells is used instrumentally with the knowledge that such an approximation only represents a first order approach to calculations. If one is doing a Hartree–Fock calculation then all the electrons are simultaneously in all the orbitals of a particular chosen configuration. As mentioned earlier this results from the permutation procedure. If one is doing C.I. then many thousands if not millions of configurations are considered in the wavefunction expansion.

Within these ab initio approaches the fact that certain elements fall into the same group of the periodic table is not explained by recourse to the number of outer-shell electrons. The explanation lies in calculating the magnitude of a property such as the first ionization energy and seeing whether the expected periodicity is recovered in the calculations. Figure 2 below shows schematically the experimental ionization energies for the first 53 elements in the periodic table, along with the values calculated using ab

initio quantum mechanical methods. As can readily be seen, the periodicity is captured remarkably well, even down to the details of the sections of the graph occurring between elements in groups II and III in each period of the table. Clearly the accurate calculation of atomic properties can be achieved by the theory. The quantum mechanical explanation of the periodic system within this approach represents a far more impressive achievement than merely claiming that elements fall into similar groups because they share the same number of outer-electrons.
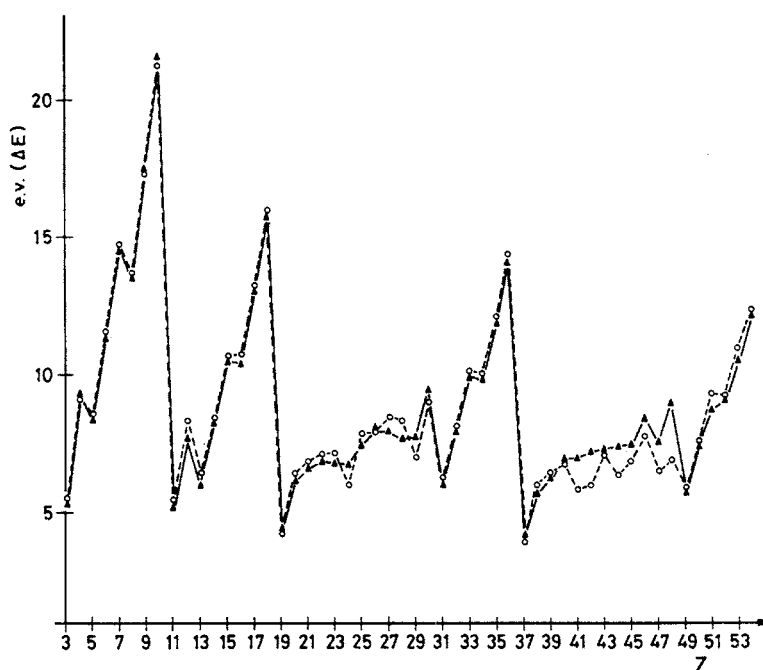
Computed (full triangles) and Experimental (open circles)

Figure 2. Comparison of computed and experimental first ionization energies for Z = 1–53.

And yet in spite of these remarkable successes such an ab initio approach may still be considered to be semi-empirical in a rather specific sense. In order to obtain calculated points shown in Figure 2 the Schrödinger equation must be solved separately for each of the 53 atoms concerned in this study. The approach therefore represents a form of 'empirical mathematics' where one calculates 53 individual Schrödinger equations in order to reproduce the well-known

pattern in the periodicities of ionization energies. It is as if one had performed 53 individual experiments, although the 'experiments' in this case are all iterative mathematical computations. This is still therefore not a general solution to the problem of the electronic structure of atoms.

13. DENSITY FUNCTIONAL APPROACH

In 1926 the physicist Llewellyn Thomas proposed treating the electrons in an atom by analogy to a statistical gas of particles. No electron-shells are envisaged in this model which was independently rediscovered by Italian physicist Enrico Fermi two years later, and is now called the Thomas–Fermi method.[16] For many years it was regarded as a mathematical curiosity without much hope of application since the results it yielded were inferior to those obtained by the method based on electron orbitals. The Thomas–Fermi method treats the electrons around the nucleus as a perfectly homogeneous electron gas. The mathematical solution for the Thomas–Fermi model is 'universal', which means that it can be solved once and for all. This should represent an improvement over the method that seeks to solve Schrödinger equation for every atom separately. Gradually the Thomas–Fermi method, or density functional theories, as its modern descendants are known, have become as powerful as methods based on orbitals and wavefunctions and in many cases can outstrip the wavefunction approaches in terms of computational accuracy.

There is another important conceptual, or even philosophical, difference between the orbital/wavefunction methods and the density functional methods. In the former case the theoretical entities are completely unobservable whereas electron density invoked by density functional theories is a genuine observable. Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques (Coppens, 2001).[17] Orbitals cannot be observed either directly, indirectly or in any other way since they have no physical reality, a state of affairs that is dictated by quantum mechanics (Scerri, 2000). Orbitals as used in ab initio calculations are mathematical figments that exist, if anything, in a multi-dimensional Hilbert space.[18] Electron density

is altogether different, as I have indicated, since it is a well-defined observable and exists in real three-dimensional space a feature that some theorists point to as a virtue of density functional methods.[19]

14. DENSITY FUNCTIONAL THEORY IN PRACTICE

Most of what has been described so far concerning density theory applies in theory rather than in practice. The fact that the Thomas–Fermi method is capable of yielding a universal solution for all atoms in the periodic table is a potentially attractive feature but is generally not realized in practice. Because of various technical difficulties, the attempts to implement the ideas originally due to Thomas and Fermi have not quite materialized. This has meant a return to the need to solve a number of equations separately for each individual atom as one does in the Hartree–Fock method and other ab initio methods using atomic orbitals. In addition most of the more tractable approaches in density functional theory also involve a return to the use of atomic orbitals in carrying out quantum mechanical calculations since there is no known means of directly obtaining the functional that captures electron density exactly.[20] Researchers therefore fall back on using basis sets of atomic orbitals which means that conceptually we are back to square one and that the promise of density functional methods to work with observable electron density has not materialized.

To make matters worse, the use of a uniform gas model for electron density does not enable one to carry out accurate calculations. Instead, 'ripples' or a density gradient, to use the more technical term, must be introduced into the uniform electron gas distribution. The way in which this has been implemented has typically been in a semi-empirical manner by working backwards from the known results on a particular atom, usually the helium atom (Gill, 1998). In this way it has been possible to obtain an approximate set of functions which often give successful approximate calculations in many other atoms and molecules. There is no known way of yet calculating, in an ab initio manner, the required degree of density gradient that must be introduced into the calculations.

By carrying out this combination of semi-empirical procedures and retreating from the pure Thomas–Fermi notion of a uniform

electron gas it has actually been possible to obtain computationally *better* results in many cases of interest than with conventional ab initio methods. True enough, calculations have become increasingly accurate but if one examines them more closely one realizes that they include considerable semi-empirical elements at various levels. From the purist philosophical point of view this means that not everything is being explained from first principles.

As time has progressed the best of both approaches (DFT and ab initio orbital methods) have been blended together with the result that many computations are now performed by a careful mixture of wavefunction and density approaches within the same computations (Hehre, 1986). This feature brings with it advantages as well as disadvantages. The unfortunate fact is that, as yet, there is really no such thing as a pure density functional method for performing calculations and so the philosophical appeal of a universal solution for all the atoms based on electron density rather than ficticious orbitals has not yet borne fruit.[21]

15. CONCLUSION

My aim has not been one of trying to decide whether or not the periodic system is explained *tout court* by quantum mechanics. Of course broadly speaking quantum mechanics does provide an excellent explanation and certainly one better than was available using only classical mechanics. But the situation is more subtle.

Whereas most chemists and educators seem to believe that all is well, I think that there is some benefit in pursuing the question of how much is strictly explained from the theory. After all, it is hardly surprising that quantum mechanics cannot yet fully *deduce* the details of the periodic table that gathers together a host of empirical data from a level far removed from the microscopic world of quantum mechanics. As Roald Hoffmann's title at this memorial meeting stated, "Most of what's interesting in chemistry is not reducible to physics" It is indeed something of a miracle that quantum mechanics explains the periodic table to the extent that it does at present. But we should not let this fact seduce us into believing that it is a complete explanation. One thing that is clear is that the attempt to explain the details of the periodic table

continues to challenge the ingenuity of quantum physicists and quantum chemists. For example, a number of physicists are trying to explain the periodic table by recourse to group theoretical symmetries in combination with quantum mechanics (Ostrovsky, 2000). Meanwhile the theoretical chemist Herschbach and colleagues have worked on a number of approaches which also aim at obtaining a global solution to the energies of the atoms in the periodic table (Kais et al., 1994)

Perhaps philosophers of chemistry have a role to play here. Unconstrained by what can presently be achieved, or even what might be achieved in the foreseeable future, one can point out the limitations of the current state of the art and one can place the research in the wider context of scientific reductionism in general and what it might mean for a calculation to be really ab initio. This is not a denial of the progress achieved in quantum chemistry or a reproach of the current work. It is more of an unrestrained look at what more could conceivably be done. Of course this might require a deeper theory than quantum mechanics or maybe a cleverer use of the existing theory. There is really no way of telling in advance.

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NOTES

[1] Another way of regarding the same question is to consider typical 'chemical explanations', full of visualizations and sometimes naïve realism, and contrast them with the more abstract mathematical explanations favored by the physicist.

[2] In fact the fourth quantum number does not emerge from solving Schrodinger's equation. It was initially introduced for experimental resons by Pauli, as a fourth degree of freedom possessed by each electron. In the later treatment by Dirac the fourth quantum number emerges in a natural manner.

[3] The fourth quantum number does not emerge from solving the Schrödinger equation.

[4] It is gratifying to see that this article has now been cited by about twelve chemistry textbooks including those by Atkins, Huheey, Levine etc.

[5] It should be noted that the Hartree–Fock method uses four quantum numbers which are given the same labels as those in the hydrogen atom. However these are not identical but only analogous. This fact is often overlooked in elementary presentations which imply that the two sets are identical.

In a recent paper Ostrovsky has criticized my claiming that electrons cannot strictly have quantum numbers assigned to them in a many-electron system (Ostrovsky, 2001). His point is that the Hartree–Fock procedure assigns all the quantum numbers to all the electrons because of the permutation procedure. However this procedure still fails to overcome the basic fact that quantum numbers for individual electrons such as l in a many-electron system fail to commute with the Hamiltonian of the system. As a result the assignment is approximate. In reality only the atom as a whole has quantum numbers, not individual electrons.

[6] Charlotte Froese Fischer was a PhD student of Hartree's in Cambridge and pioneered accurate calculations using the method initially devised by Hartree.

[7] Admittedly Hartree–Fock calculations whether relativistic or not omit correlation effects in atoms since they involve time averages of electron repulsions.

[8] Broadly speaking it is still an orbital based method of course but not one that corresponds to the elementary concept of a particular number of electrons in the shells of an atom.

[9] In fact given that the C.I. approach involves a mixture of so many different configurations it is capable of calculating the energy of the entire atom but not specifically of the ground state configuration.

[10] The CISD method produces typical errors of 0.4–0.7 eV for the ground states of elements from manganese to copper even after the inclusion of relativistic effects. The Coupled Cluster method called CPF produces an error of 0.4 eV for the d^8s^2 to d^9s^1 splitting in nickel. The basis set cited in the main text comes from a study in which an elaborate quadratic CI method was used in which the already large basis set was augmented with numerous 'diffuse' orbitals (Raghavachari and Trucks, 1989). The use of M-P perturbation theory produced what the authors of this article describe as "wild oscillations" for the same excitation energy.

[11] I am doing a certain amount of back-tracking given that this method was mentioned above when some results were quoted for transition metals.

[12] In fact there are some other good reasons to support the placement of helium in the alkaline earths, contrary to popular opinion among chemists as I will be exploring in a forthcoming article.

[13] Although as noted the configuration of Ni is actually $4s^1 3d^9$ contrary to what is stated in most textbooks.

[14] The question for realism is altogether different if taken in the sense of the belief in unobservable scientific entities. In fact many philosophers of science currently favor some form of scientific realism in the context of quantum mechanics (Cao, 2003).

[15] So I advocate realism about chemical reactions that can be observed macro-scopically without being a realist about electrons in shells.

[16] But Teller showed that the Thomas–Fermi model cannot predict binding in atoms.

[17] This is why I and some others have been agitating about the recent reports, starting in Nature magazine in September 1999, that atomic orbitals had been directly observed. This is simply impossible (Scerri, 2000).

[18] I have tried to stress the educational implications of the claims for the observation of orbitals in other articles and will not dwell on the issue here (Scerri, 2000, both articles cited for that year).

[19] Of course it is a matter of taste whether one uses ficticious orbitals or real and observable electron density.

[20] Promise due to theorems proved by Hohenberg and Sham and Kohn.

[21] Some preliminary work aimed at developing pure density methods has been carried out (Wang and Carter, 2000).

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