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THE PERIODIC TABLE

Its Story and Its Significance

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CHAPTER
9

QUANTUM MECHANICS AND THE PERIODIC TABLE

In chapter 7, the influence of the old quantum theory on the periodic system was considered. Although the development of this theory provided a way of reexpressing the periodic table in terms of the number of outer-shell electrons, it did not yield anything essentially new to the understanding of chemistry. Indeed, in several cases, chemists such as Irving Langmuir, J.D. Main Smith, and Charles Bury were able to go further than physicists in assigning electronic configurations, as described in chapter 8, because they were more familiar with the chemical properties of individual elements. Moreover, despite the rhetoric in favor of quantum mechanics, that was propagated by Niels Bohr and others, the discovery that hafnium was a transition metal and not a rare earth was not made deductively from the quantum theory.¹ It was essentially a chemical fact that was accommodated in terms of the quantum mechanical understanding of the periodic table.

The old quantum theory was quantitatively impotent in the context of the periodic table since it was not possible to even set up the necessary equations to begin to obtain solutions for the atoms with more than one electron. An explanation could be given for the periodic table in terms of numbers of electrons in the outer shells of atoms, but generally only after the facts. But when it came to trying to predict quantitative aspects of atoms, such as the ground-state energy of the helium atom, the old quantum theory was quite hopeless. As one physicist stated, "We should not be surprised . . . even the astronomers have not yet satisfactorily solved the three-body problem in spite of efforts over the centuries."² A succession of the best minds in physics, including Hendrik Kramers, Werner Heisenberg, and Arnold Sommerfeld, made strenuous attempts to calculate the spectrum of helium but to no avail.

It was only following the introduction of the Pauli exclusion principle and the development of the new quantum mechanics that Heisenberg succeeded where everyone else had failed. In fact, Heisenberg performed the calculation using both

his own matrix mechanics and Erwin Schrödinger's wave mechanics as discussed below. In terms of wave mechanics, Heisenberg interpreted his result as showing the need for the overlap between the wavefunctions of the two electrons in helium. This overlap, which he called an "exchange term," was due entirely to the indistinguishability of the two electrons. This meant that the terms in the equation had to be written in two ways, the second of which involved the exchange of labels to account for the fact that both electrons are identical. Such exchange terms³ are highly nonclassical and follow from Wolfgang Pauli's discovery of the exclusion principle.

This discovery was to be the beginning of the use of exchange terms in the quantum mechanics of atoms and molecules. It became the key factor that shortly afterward allowed Walter Heitler and Fritz London to obtain the first successful quantum mechanical calculation of the covalent bond in the simplest case of a diatomic hydrogen molecule. Exchange terms would also pave the way for the notion of quantum mechanical resonance and the development of the quantum mechanical theories of bonding by Linus Pauling and many others.⁴

Perhaps the key advance that quantum mechanics provided, compared with the old quantum theory, was that the quantization itself seemed to arise in a more natural manner. In the old quantum theory, Bohr had been forced to postulate that the angular momentum of electrons was quantized, while the advent of quantum mechanics showed that this condition was provided by the theory itself and did not have to be introduced by fiat. For example, in Schrödinger's version of quantum mechanics, the differential equation is written, and certain boundary conditions are applied, with the result that quantization emerges automatically.

A conceptual grasp for how the application of boundary conditions to waves leads naturally to quantization can be obtained from the following analogy. Suppose that a string is tied at both ends and made to vibrate. It turns out that the string can adopt one of many possible standing wave patterns where certain points along the string remain stationary. As shown in figure 9.1, the string can vibrate either as a whole or with a number of so-called nodes, each of which represents a stationary point along the string.

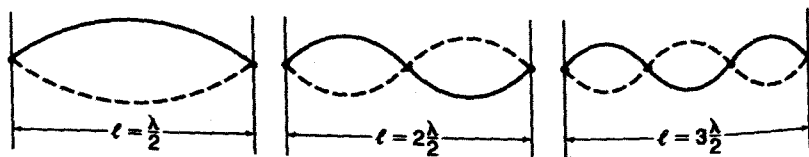


FIGURE 9.1 The imposition of boundary conditions produces quantization in a vibrating wave. From R. Chang, *Physical Chemistry for the Chemical and Biological Sciences*, University Science Books, Sausalito, CA, 2000, p. 576. By permission from the publisher.

In other words, the mere presence of waves that are bound at both ends immediately implies quantization of the form described above. The string can vibrate only in a number of well-defined ways that have 0, 1, 2, 3, and so on, nodes. No other intermediate vibrational nodes can exist, and this is the essence of quantization associated with any kind of standing wave phenomenon.

FROM BOHR'S OLD QUANTUM THEORY TO QUANTUM MECHANICS

What Bohr had been doing in his explanations of the periodic table was not deducing electronic configurations from first principles, as he led his readers to believe; rather, he was essentially working backward from chemical and spectroscopic facts and showing that these facts were consistent with a quantum theoretical description.

But the old quantum theory was only the beginning of quantum mechanics, which is the most powerful physical theory that has ever been devised. The transition between the old quantum theory and the new quantum mechanics is examined in this chapter, as is the impact that the updated theory had on attempts to understand the periodic table. As I argue here, the effect has been considerable, but surprisingly still incomplete, from the fundamental point of view of trying to provide a deeper explanation of the periodic system. Nevertheless, many forms of more accurate calculations can now be carried out in quantum chemistry than were even dreamt of at the time of the old quantum theory.

Although it is not my intention to give a history of the transition between Bohr's old quantum theory and the later quantum mechanics, it is necessary to sketch some of the steps that were taken. In fact, one of the connecting steps between the old and the new versions of quantum theory is mentioned in chapter 7, because it provided the culminating step in the explanation of the periodic system as it is still generally understood. This was the introduction by Pauli of the fourth quantum number and his subsequent discovery of the Pauli exclusion principle, which dictates that no two electrons in an atom can possess the same four quantum numbers. What follows from this assumption is an elegant explanation of the possible lengths of any period but only provided that one is willing to admit some experimental information into the explanation.

As noted in chapter 7, an explanation can be given for the maximum possible number of electrons in any shell around the nucleus. The formula $2n^2$, which had been recognized for some time as summarizing the number of elements in any particular period, is thus given an apparent theoretical underpinning. But there is one aspect, the order of shell filling, that has not yet been deduced from first principles. This issue cannot be avoided if one is to really ask whether quantum mechanics explains the periodic system in a fundamental manner.

THE ADVENT OF QUANTUM MECHANICS

The old quantum theory reached a crisis point around 1924–1925, at which time it was realized that a more radical theory would be needed in order to settle a number of outstanding problems in physics. One of these problems of particular importance to the story of the periodic table was the attempt to calculate the properties of helium, the second atom in the periodic table following hydrogen. Whereas the old quantum theory provided a means of obtaining an exact solution to the calculation of the energy of the hydrogen atom, the move to considering helium appeared to cause insurmountable problems. It was not that the solution of this problem was just difficult in the old quantum theory. It was not even possible to formulate the necessary equations adequately.

Only following the advent of quantum mechanics, as distinct from the old quantum theory, was there a possibility of calculating the energy of helium, and even then only approximately. Developments initially occurred along two distinct lines. First of all, Heisenberg, a very young German, developed an approach that eventually became known as matrix mechanics. Heisenberg's original motivation appears to have been the complete abandonment of unobservable features of the world, such as atomic orbits.⁵ This followed the realization that atomic orbits were quite different from the orbits of planets and other macroscopic objects. They were eventually renamed "orbitals" instead of orbits, a name intended to mean a form of motion without a definite trajectory. Unfortunately, the change in terminology is too subtle, with the result that many chemists, in particular, still seem to maintain some form of pathlike visualization.⁶

Heisenberg intended to build a theory centered on observable quantities such as spectral frequencies. The theory that he developed was highly counterintuitive and required physicists to invest much time and effort in learning a new branch of mathematics dealing with the manipulation of matrices. In addition, the attempt to reject unobservable quantities that Heisenberg had hoped for was not realized.

At about the same time, Schrödinger developed what came to be known as wave mechanics. Already in 1924, the French physicist Prince Louis De Broglie had suggested an analogy to Albert Einstein's earlier discovery that light waves have a particulate nature as well as their expected wave nature. De Broglie made the association run in the opposite sense. Why not suppose that particles such as electrons could likewise display wavelike properties? The test for this idea would be to demonstrate experimentally that electrons produce diffraction and interference effects just like classical waves, such as waves on the surface of water.⁷

Two physicists, Clinton Davisson and Lester Germer, successfully carried out just such an experiment in 1927, thus giving experimental support to De Broglie's proposal.⁸ With this discovery, theorists such as Schrödinger received the impetus to further pursue the mathematical analogies between classical waves and electron waves.⁹ Whereas Heisenberg's approach was mathematically abstract, that of

Schrödinger was more familiar to physicists because it dealt principally with wave motion. Unlike Heisenberg, Schrödinger had not originally tried to break with realistic notions of the microscopic world and, in fact, had hoped that his method would retain strong connections with classical physics and physical visualization.

As it turned out, neither Heisenberg's nor Schrödinger's hopes materialized fully. The quantum mechanics that emerged after a few years of intense debate was not based solely on observable properties, and nor was it possible to retain a realistic view of matter waves as Schrödinger had originally hoped. Moreover, the two forms of quantum mechanics were shown to be equivalent.¹⁰

The new theory became centered on the wavefunction for an atom or molecule. This wavefunction could be expressed with a number of terms called "atomic orbitals." As mentioned above, the name was derived from atomic orbits of the old quantum theory but without any intended connection with a definite trajectory for the electron. Such orbitals inhabit a multidimensional Hilbert space in quantum mechanics, thus further denying their visualizability in familiar three-dimensional space. Moreover, wavefunctions and their component building blocks consisting of such orbitals are themselves complex mathematical functions in the sense that they contain factors involving the square root of -1 .

What is observable in the case of wavefunctions, as it emerged a little later, is the square of the wavefunction,¹¹ which is called the electron density.¹² In addition, even the square of the wavefunction cannot be obtained for a single electron at a specific point. The interpretation of quantum mechanics calls for a statistical view in which one can know only the probability of an electron residing in a certain region of space.

HARTREE-FOCK METHOD

When it comes to calculating the properties of atoms, the new quantum mechanics provides a way in which the problem can be attacked by means of approximation methods.¹³ The basis of the most widely used approximation for solving quantum mechanical equations for atoms is called the Hartree-Fock method after Douglas Hartree (figure 9.2) and Vladimir Fock, an English and a Russian physicist, respectively.¹⁴

The main assumption made in the Hartree-Fock model is that any given electron moves in a field resulting from the attraction of the nucleus added to the field that results from the sum of all the remaining electrons. This approach avoids dealing directly with individual electron-electron repulsion terms, and instead, one recovers a situation not altogether unlike that of the hydrogen atom in which one electron is moving is a spherically symmetrical field. In the many-electron case, the field consists of those of the nucleus and of all the other electrons lumped together. The only difference is that instead of one equation for one electron, there



FIGURE 9.2
Douglas Hartree. Photo
and permission from
Emilio Segrè Collection.

are now as many equations as there are electrons in the atom. In addition, the solution for each electron must be consistent with those for all the other electrons, thus requiring a self-consistent iteration procedure that is typically carried out on a computer.

But let us return to the question the explanation of periodicity, which opened this chapter. The Pauli exclusion principle and the use of four quantum numbers only provide a deductive explanation of the total number of electrons that any electron shell can hold. The correspondence of these values with the number of elements that occur in any particular period is something of a coincidence. The lengths of successive periods have not yet been strictly deduced from the theory.¹⁵ However, most chemistry and physics textbook authors do not emphasize or even mention this point. As a result, they imply that quantum mechanics does indeed provide a perfectly satisfactory deductive explanation of the periodic system. This, in turn, fuels the general impression that chemistry is fully explained by quantum physics and has a negative effect on chemical education. Instead of starting from chemical facts, and the properties of the elements, the modern tendency is to expose students to the rules for electronic configurations in the belief that the chemistry will somehow follow.¹⁶ Nevertheless, the number of electrons contained in any shell, as opposed to the lengths of periods, does emerge directly from the rules for combining the four quantum numbers. This part of the explanation for periodicity is completely satisfactory, as shown in the next section.

WRITING ELECTRONIC CONFIGURATIONS FOR ATOMS

The assignment of electronic configurations to the atoms in the periodic table proceeds according to three principles:

1. The *aufbau* principle (*aufbauprinzip* in chapter 7): Orbitals are occupied in order of increasing values of $n + \ell$. For example, the 4s orbital for which $n + \ell = 4$ is filled before the 3d orbital for which $n + \ell = 5$. This rule is often accompanied by a diagram like the one shown in figure 9.3, which represents the Madelung or $n + \ell$ rule.
2. The Hund principle: When electrons fill orbitals of equal energies, they occupy as many different orbitals as possible.
3. The Pauli exclusion principle: Only two electrons can occupy a single orbital, and if they do so they must orient their spin angular momenta in opposite directions.¹⁷

Several points need to be made about these principles. The first principle does not, in fact, refer to the ordering of energies of atomic orbitals. What it really refers to is the order of filling of the various orbitals. These are related but separate issues. But there is more involved in the occupation of orbitals than their individual energies, as discussed further below. The $n + \ell$ rule has not yet been derived from the principles of quantum mechanics. This failure has been described as one of the outstanding problems in quantum mechanics by the leading quantum chemist Per-Olav Löwdin.¹⁸

It emerges that all three of these principles are essentially empirical, and none of them has been strictly derived from the principles of quantum mechanics.¹⁹ Pauli's principle, for example, takes the form of an additional postulate to the main postulates of quantum mechanics. Despite strenuous efforts on the part of many physicists, including Pauli himself, it has never been possible to derive the principle from the postulates of quantum mechanics and/or relativity theory.²⁰ So, rather

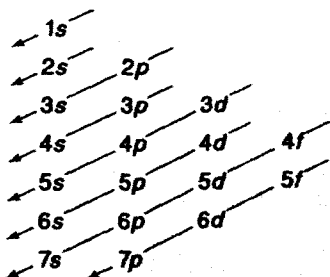


FIGURE 9.3
Madelung (or $n + \ell$) rule
for the order of filling of
orbitals. From R. Chang,
*Physical Chemistry for the
Chemical and Biological
Sciences*, University Science
Books, Sausalito, CA, 2000,
p. 601. By permission from
the publisher.

than providing an explanation for electronic configurations, the three commonly used rules are really statements that summarize what is known to happen from experimental data on atomic spectra.

And now let us turn to the explanation for the number of electrons in each shell and its connection to the number of elements in each subsequent period of the periodic table. These facts are usually explained in terms of the relationship between the four quantum numbers, which can be assigned to any electron in a many-electron atom. The relationship between the first three quantum numbers is rigorously deduced from the Schrödinger equation for the hydrogen atom. The first quantum number, n , can adopt any integral value starting with 1.²¹ The second quantum number, which is given the label ℓ , can have any of the following values related to the values of n :

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

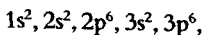
In the case when $n = 3$, for example, ℓ can take the values 2, 1, or 0. The third quantum number, labeled m_ℓ , can adopt values related to those of the second quantum numbers:

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

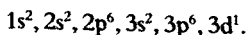
For example, if $\ell = 2$ the possible values of m_ℓ are $-2, -1, 0, +1$, and $+2$. Finally, the fourth quantum number, labeled m_s , can take only two possible values, either $+1/2$ or $-1/2$ units of spin angular momentum. There is therefore a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom.

As a result of this scheme, it is clear why the third shell, for example, can contain a total of 18 electrons. If the first quantum number, given by the shell number, is 3, there will be a total of $2 \times (3)^2$ or 18 electrons in the third shell.²² 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 2 since the fourth quantum number can adopt values of $1/2$ or $-1/2$.

But the fact that the third shell can contain 18 electrons does not strictly explain why it is that some of the periods in the periodic system contain 18 places. It would be a rigorous explanation of this fact only if electron shells were filled in a strictly sequential manner. Although electron shells begin by filling in a sequential manner, this ceases to be the case starting with element 19, potassium. Since the configuration of element 18, argon, is



one might expect the configuration for element 19, potassium, would be



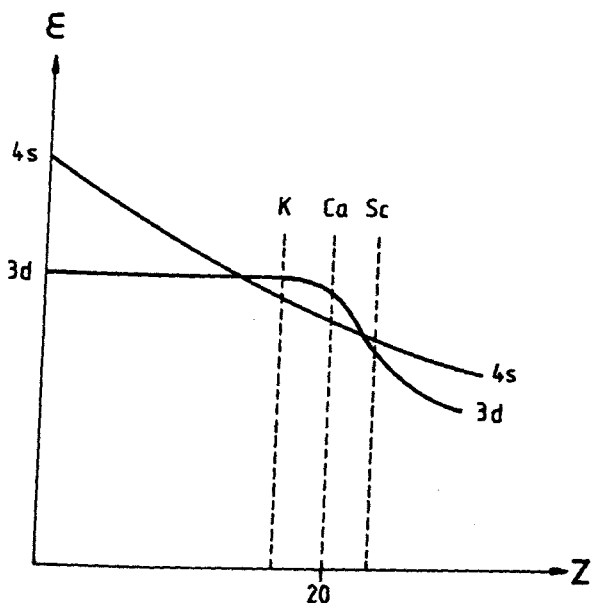
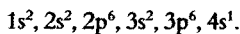


FIGURE 9.4 The relative ordering of the 3d and 4s energy levels. L.G. Vanquickenborne, K. Pierloot, D. Devoghel, *Journal of Chemical Education*, 71, 469–471, 1994, p. 469. By permission from the publisher.

This would be expected because up to this point the pattern has been one of adding the differentiating electron to the next available orbital at increasing distances from the nucleus. However, experimental evidence shows that the configuration of potassium should be denoted as



As many textbooks explain, this can result from the fact that the 4s orbital has a lower energy than the 3d orbital for the atoms of potassium and calcium (see figure 9.4).

In the case of element 20, calcium, the new electron also enters the 4s orbital. But in the case of element 21, scandium, the orbital energies have reversed so that the 3d orbital has a lower energy. Textbooks typically claim that since the 4s orbital is already full, the next electron necessarily begins to occupy the 3d orbital. This pattern is supposed to continue across the first transition series of elements, apart from the elements chromium and copper, where further anomalies occur (table 9.1).

In fact, this explanation for the configuration of the scandium atom, and most other first transition elements, is inconsistent.²³ If the 3d orbital has a lower energy

TABLE 9.1
Electronic Configurations for
First Transition Metals

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

than 4s starting at scandium, and if one were indeed filling the orbitals with electrons in order of increasing energy, one would expect that all three of the final electrons would enter 3d orbitals. The argument that 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. One should not have to consider the configuration of the previous element and assume that this configuration is somehow carried over intact on moving to the next element.

What seems to make this issue more mysterious is that, whereas all transition elements show a preferential occupation for an s orbital, it appears that the s electrons are also the easiest to ionize. This situation may be represented by two diagrams, one for relative occupation and one for relative ionization of orbitals in the first transition series, to give the sets of ordered levels shown in figure 9.5.

The apparent paradox is as follows: If the 4s orbital is preferentially occupied by electrons, this suggests that it has greater stability after all interactions have been properly taken into account.²⁴ However, the right diagram in figure 9.5, which depicts the relative ease of losing electrons, suggests that the 4s electrons are overall less stable since they, rather than the 3d electrons, are more easily removed. Many complicated analyses of this situation have been published in recent years in order to try to resolve the apparent paradox.²⁵

There is perhaps a simple solution, or perhaps a dissolution, of the problem. In posing the paradox regarding the 4s and 3d orbitals, many authors appear to have overlooked one very important feature, which makes the comparison problematic. In considering the buildup of atoms across the periodic table, one is concerned with the successive addition of one proton and one electron to each previous atom.²⁶ However, in considering the ionization of any particular atom, one is concerned only with the successive removal of electrons and not the removal



Filling of orbitals

ionization of orbitals

FIGURE 9.5 Ordering of orbital energies as implied by relative filling and relative ionization. The lower the level, the more stable the atom.

of protons. As a result, the comparison of the two diagrams in figure 9.5 does not constitute a comparison of like with like. The long-standing puzzle, which has exercised the minds of generations of students and their instructors, can be dissolved at a stroke. The question of why 4s fills first but also empties first is an illegitimate question in some respects.

AN EXPLANATION FOR SHELL CLOSING BUT NOT FOR PERIOD CLOSING

As suggested above, there is a problem with the claim that the periodic table is deductively explained by quantum mechanics. A feature that seems to generally go unnoticed is the need to assume the empirical order of shell filling rather than trying to derive it from the theory. The order in which orbitals are occupied with electrons is not derived from first principles. It is justified *post facto* and by some complex calculations.

Suppose, for example, that the Hartree-Fock method is used to compare the energies of the scandium atom with two alternative configurations: $[\text{Ar}] 4s^2 3d^1$ and $[\text{Ar}] 4s^1 3d^2$. This can be carried out using ordinary nonrelativistic quantum mechanics or, alternatively, by including relativistic effects. The results obtained are as shown in table 9.2.²⁷ In each case, the more negative the calculated value of the energy, the more stable the configuration.²⁸ Clearly, the inclusion of relativistic effects serves to reduce the energy from the nonrelativistic value, as one would expect. In the case of scandium, it appears that both nonrelativistic and relativistic *ab initio* calculations correctly compute that the $4s^2$ configuration has the lower energy, in accordance with experimental data. Similar calculations do not fare so well in the case of the chromium atom, however (table 9.3). In this case, it appears that both nonrelativistic and relativistic calculations fail to predict

TABLE 9.2
 Nonrelativistic and Relativistic Calculated
 Energies for Two Configurations of Scandium
 (in Hartree units)

<i>4s² 3d¹ configuration</i>	
Nonrelativistic	-759.73571776
Relativistic	-763.17110138
<i>4s¹ 3d² configuration</i>	
Nonrelativistic	-759.66328045
Relativistic	-763.09426510

One Hartree is equal to 4.3597×10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, one of the leading pioneers in the field of Hartree-Fock calculations. <http://atoms.vuse.vanderbilt.edu/>

TABLE 9.3
 Nonrelativistic and Relativistic Calculated
 Energies for Two Configurations of Chromium
 (in Hartree units)

<i>4s¹ 3d⁵ configuration</i>	
Nonrelativistic	-1043.141755
Relativistic	-1049.24406264
<i>4s² 3d⁴ configuration</i>	
Nonrelativistic	-1043.17611655
Relativistic	-1049.28622286

One Hartree is equal to 4.3597×10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, <http://atoms.vuse.vanderbilt.edu/>

which of these two configurations is the correct experimentally observed ground state, namely, $4s^1 3d^5$.

Looking at the calculated energies for the copper atom in table 9.4 shows that a nonrelativistic calculation sometimes gives the correct result for the lowest energy configuration. However, it also emerges that by carrying out the calculation to a greater degree of accuracy by including relativistic effects the prediction can in some cases deteriorate in that one predicts the opposite order of stabilities than observed experimentally. The lowest energy configuration for copper cannot yet be successfully calculated from first principles, at least at this level of approximation.

TABLE 9.4
 Nonrelativistic and Relativistic Calculated
 Energies for Two Configurations of Copper
 (in Hartree units)

<i>4s¹3d¹⁰ configuration</i>	
Nonrelativistic	-1638.9637416
Relativistic	-1652.66923668
<i>4s²3d⁹ configuration</i>	
Nonrelativistic	-1638.95008061
Relativistic	-1652.67104670

One Hartree is equal to 4.3597×10^{-18} J.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, <http://atoms.vuse.vanderbilt.edu/>

The fact that copper has a $4s^1 3d^{10}$ configuration rather than $4s^2 3d^9$ is an experimental fact. The theory is, strictly speaking, accommodating what is already known experimentally. For example, the first of the two periods of 18 elements 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. This coincidence is what gives the generally given explanation its apparent credence. It does not seem to be appreciated that these are not the same 18 electrons that are "doing the occupying" as one traverses the periodic table.²⁹

The Nickel Atom

The case of nickel turns out to be more interesting (table 9.5). 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 invariably quotes the configuration of nickel as $4s^1 3d^9$. The difference occurs because in more accurate work one considers not just the lowest possible component of the ground-state term but the average of all the components arising from a particular configuration. Nickel is somewhat unusual in that, although the lowest energy term arises from the $4s^2 3d^8$ configuration, the average energy of all the components arising from this configuration is higher than the average energy of all the components arising from the $4s^1 3d^9$ configuration. As a consequence, the $4s^2 3d^8$ configuration is regarded as the ground state, and it is this average energy that is compared with experimental energies. When this comparison is made, it emerges that the quantum mechanical calculations using a relativistic Hartree-Fock approach give an incorrect ground state.

TABLE 9.5
 Nonrelativistic and Relativistic Calculated
 Energies for Two Configurations of Nickel
 (in Hartree units)

4s²3d⁸ configuration

Nonrelativistic -1506.87090774

Relativistic -1518.68636410

4s¹3d⁹ configuration

Nonrelativistic -1506.82402795

Relativistic -1518.62638541

One Hartree is equal to 4.3597×10^{-18} J. Note that theory predicts a 4s² 3d⁸ configuration.

Compiled by the author. These results were obtained using the Internet web pages designed by Charlotte Froese-Fischer, <http://atoms.vuse.vanderbilt.edu/>

Of course, the calculations can be improved by adding extra terms until this failure is eventually corrected, but these additional measures are taken only after the fact. Moreover, 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 this context.³⁰

Back to Hund's Rule

Let us now consider the Hund principle and the manner in which it is used to justify the configurations of elements in the first, second, and third transitions. The elements in the first transition are generally believed to show two "anomalous" configurations, which include a 4s¹ orbital occupation, rather than the more common 4s² configuration.³¹ These atoms are those of chromium and copper, which are taken to have respective configurations of 4s¹ 3d⁵ and 4s¹ 3d¹⁰. The justification for the adoption of the first of these configurations is frequently given by appeal to Hund's rule of maximum spin multiplicity. It is argued that this configuration is more stable than any alternatives because it involves a half-filled d subshell. However, if the configurations of the elements in the second transition series are considered, it is clear that this form of explanation is rather ad hoc in the sense that it cannot be generalized to other transition series.

For example, the configurations of the elements in the second transition series are shown in table 9.6. Once again, this set of configurations is primarily arrived at from experimental data, although these ground-state configurations are supported

TABLE 9.6
Configurations of Outermost
Two Orbitals of Elements in
Second Transition Series

Y	$5s^24d^1$
Zr	$5s^24d^2$
Nb	$5s^14d^4$
Mo	$5s^14d^5$
Tc	$5s^14d^6$
Ru	$5s^14d^7$
Rh	$5s^14d^8$
Pd	$5s^04d^{10}$
Ag	$5s^14d^{10}$
Cd	$5s^24d^{10}$

by theoretical calculations in most cases. But if the possession of half-filled orbitals is the explanation for why chromium adopts a $4s^1$ configuration in the first transition series, some other factors must be operating in many cases of the second transition. This is because many of these atoms likewise show an s^1 configuration even though they do not possess a half filled d subshell.³² Hund's principle is essentially an empirical result. In spite of many attempts, nobody has yet succeeded in deriving the principle from quantum mechanics.³³ Of course, some plausible arguments can be given for its effectiveness, such as the claim that one is thereby minimizing the contribution from exchange terms involving repulsions between electrons. For example, a calculation can be carried out to show that, in the case of the helium atom, the triplet state (one involving two unpaired electrons) has lower energy than the singlet state where the two electrons are paired. But contrary to the standard account one encounters in textbooks, it has been shown that the reason for the greater stability of the helium triplet state is not reduced electron-electron repulsion but the greater electron-nucleus attraction that occurs in the triplet state.³⁴

Choice of Basis Set

There is yet another general problem that mars any hope of claiming that electronic configurations can be predicted theoretically and that quantum mechanics thereby provides a purely deductive explanation of what was previously only obtained from experiments. In most of the configurations considered above, it has been possible to use quantum mechanics to calculate the particular configuration that possesses the lowest energy. However, in performing such cal-

culations, the candidate configurations that are subjected to the calculation are themselves obtained from the *aufbau* principle and other rules of thumb such as Hund's principle, or by straightforward appeal to experimental data. Theoretical calculations cannot actually predict the electronic configuration for any element. There is a very simple reason for this state of affairs, which is often overlooked. The quantum mechanical calculations on ground-state energies involve the initial selection of a basis set, which in simple terms is the electronic configuration of the atom in question. Quantum mechanical calculations do not actually generate their own basis sets.³⁵ So, whereas the correct ground-state electronic configurations can in many cases be correctly calculated among a number of plausible options, the options themselves are not provided by the theory. This is another weakness of the present claims to the effect that quantum mechanics fully explains the periodic system, although this limitation is being addressed in some recent work.

THREE POSSIBLE APPROACHES TO THE REDUCTION OF THE PERIODIC TABLE

This section attempts to take stock of the various senses of the claim that the periodic system is reduced, or fully explained, by quantum mechanics.

Qualitative Reduction/Explanation of Periodic Table in Terms of Electrons in Shells

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 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 such as the ground-state energy of any particular atom. In order to do so, one needs to go beyond the ground-state configuration of the atom in question, and it is essential to assume that electrons also find themselves in higher energy orbitals that are not considered in the textbook configuration of the element.

In addition, 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 generally placed among the alkaline earth elements such as magnesium, calcium, and barium, all of which also display two outer-shell electrons.³⁶

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 among the transition metal series. Consider this interesting example:³⁷

Ni	[Ar] 4s ² 3d ⁸
Pd	[Kr] 5s ⁰ 4d ¹⁰
Pt	[Xe] 6s ¹ 4f ¹⁴ 5d ⁹

In addition, the very notion of a particular number of electrons in a particular shell stands in violation of the Pauli exclusion principle, which states that electrons cannot be distinguished.³⁷ The indistinguishability of electrons implies that one can never state that a particular number of electrons are in any particular shell, although it is frequently useful to make this approximation. Indeed, the independent-electron approximation, as it is known, represents one of the central paradigms in modern chemistry and physics. To state the electronic configuration of an atom is to operate within this level of approximation. For example, one might state that the configurations of two randomly chosen elements are as follows:

Carbon	1s ² , 2s ² , 2p ²
Fluorine	1s ² , 2s ² , 2p ⁵

This kind of activity could only be considered as fully satisfactory and as indicating a theoretical deduction if such configurations themselves could be derived from quantum mechanics. However, as discussed above, electronic configurations such as those for carbon and fluorine are arrived at essentially by means of the *aufbau* principle, which is experimentally based. The configurations can be justified in terms of calculations in some cases, but they cannot be derived from first principles because the basis set, consisting of a particular set of atomic orbitals, is generally selected before any calculation can be carried out.

Ab Initio Calculations

The second approach to be considered is a far better candidate for the claim to explain the periodic table from quantum mechanics. Even if the crude notion of a particular number of outer-shell electrons for any particular atom fails to give a fundamental explanation, it should be possible to carry out detailed calculations that allow atoms to have more complicated configurations. Going to such a deeper level than the notion of a particular number of electrons in shells might thus provide a more successful explanation of the periodic system.

Ab initio calculations aim to calculate the properties of atoms and molecules starting from the fundamental equation of quantum mechanics, the Schrödinger

equation for the system. The various methods utilized vary in the extent to which they are genuinely *ab initio*. In some cases, the methods incorporate semiempirical aspects. For example, certain integration terms that are too difficult to evaluate are replaced by quantities derived from experimental data. But the type of approach considered here is the purer variety of such calculations, where no semiempirical aspects are incorporated. My aim is to examine the extent to which such *ab initio* approaches provide a reduction of the periodic system.

Such an approach represents an improvement and is a better contender for the claim of a full explanation of the periodic system. In order to illustrate both the power and the pitfalls of the method, I focus 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 represents only a first-order approach to calculations. If one wishes to still think in terms of electrons in orbitals, these calculations can be thought of as regarding the atom as existing in many different electronic configurations simultaneously. The ground-state configuration, so beloved of chemistry and physics textbooks, is just the leading term in an algebraic expansion for the wavefunction of the atom in question.³⁹

At this level of approximation, 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. Instead, 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 9.6 shows schematically the experimental first-ionization energies for elements 3–53 in the periodic table, along with the values calculated using *ab initio* quantum mechanical methods. As is readily apparent from the figure, the periodicity is captured remarkably well, even down to portions of the graph occurring between elements in groups II and III and between groups V and VI in each period of the table. Clearly, the calculation of atomic properties can be achieved by the theory to a high degree of accuracy. 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.

And yet in spite of these remarkable successes, such an *ab initio* approach may still be considered to be semiempirical in a rather specific sense. In order to obtain the calculated points shown in figure 9.6, the Schrödinger equation must be solved separately for each of the 50 atoms concerned. The approach therefore represents a form of “empirical mathematics,”⁴⁰ where one solves 50 individual Schrödinger equations in order to reproduce the well-known pattern in the periodicities of ionization energies. It is as if one had performed 50 individual experiments, although the “experiments” in this case are all iterative mathematical

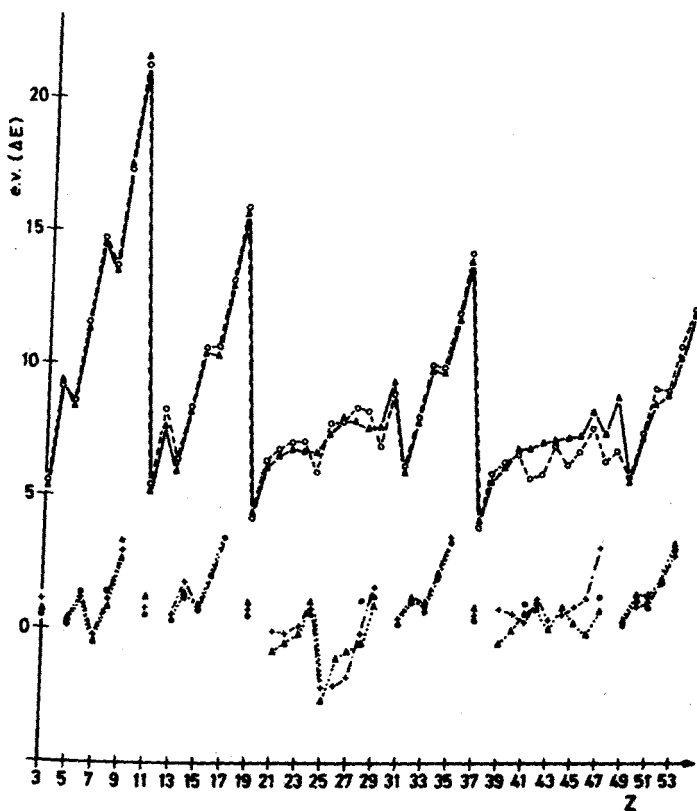


FIGURE 9.6 Calculated and observed first ionization energies of elements 3–53. Ionization energy is plotted against atomic number. Circles represent experimental values; triangles are calculated values From E. Clementi, *Computational Aspects of Large Chemical Systems, Lecture Notes in Chemistry*, vol. 19, Springer-Verlag, Berlin, 1980, p. 12. By permission from the publisher.

computations. This is still, therefore, not a general solution to the problem of the electronic structure of atoms.

Density Functional Approach

The third kind of approach to reducing the periodic table does not suffer from the drawback just mentioned in the case of *ab initio* calculations, at least not in principle. 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, although electrons still possess angular momentum values as they do

in the electron-shell model. This method was independently rediscovered by Italian physicist Enrico Fermi two years later, and is now called the Thomas-Fermi method. For many years, it was regarded as a mathematical curiosity without applications since the results it yielded were inferior to those obtained by the method based on electron orbitals. The appeal of the Thomas-Fermi method comes from the fact that it treats the electrons around the nucleus as a perfectly homogeneous electron gas and that the mathematical solution for this system is "universal" in the sense that it can be solved once and for all. This represents an improvement over any method in which one seeks to solve a Schrödinger equation for every separate atom as in the wavefunction approach illustrated in figure 9.6.

Gradually, the Thomas-Fermi method or its modern descendants, which are known as density functional theories, have become equally powerful compared to methods based on orbitals and wavefunctions and in many cases can outstrip the wavefunction approaches in terms of computational accuracy. The solution is expressed in terms of the variable Z , which represents atomic number, the crucial feature that distinguishes one kind of atom from any other element. One does not need to repeat the calculation separately for each atom, but this advantage applies only in principle, as discussed below.

There is another important conceptual, or even philosophical, difference between the orbital/wavefunction methods and the required density functional methods. In the case of orbitals, the theoretical entities are completely unobservable, whereas electron density, which is featured in density functional theories, is a genuine observable.⁴¹ Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques.⁴² Orbitals cannot be observed either directly or indirectly since they have no physical reality, a state of affairs dictated by quantum mechanics. The orbitals used in *ab initio* calculations are just mathematical constructs that exist in a multidimensional Hilbert space,⁴³ while electron density is altogether different, as indicated, since it is a well-defined observable and exists in real three-dimensional space.⁴⁴

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 has not been realized in practice. Because of various technical difficulties, which are not described here, the attempts to implement the ideas originally due to Thomas and Fermi have not materialized.⁴⁵ 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 obtaining the functional based directly on electron density.⁴⁶ Researchers therefore fall back on using basis sets of atomic orbitals that yield the electron density when squared.

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" must be introduced into the uniform electron gas distribution. The way in which this has been implemented has typically been in a semiempirical manner by working backward from the known results on a particular system, usually taken to be the helium atom. In this way, it has been possible to obtain an approximate set of functions that also give successful approximate calculations in many other atoms and molecules. By carrying out this combination of a semiempirical approach and retreating from the pure Thomas-Fermi ideal of a uniform gas, it has actually been possible to obtain computationally better results, in many cases, than with conventional ab initio methods using orbitals and wavefunctions.⁴⁷

If anything, the early promise and hope offered by quantum mechanics and Paul Dirac's famous dictum that all of chemistry can be calculated from first principles has turned out to be only partly fulfilled.⁴⁸ Although calculations have become increasingly accurate, one realizes that they include considerable semiempirical elements at various levels. From the purist philosophical point of view, this implies that not everything is being explained from first principles.

As time has progressed, the best of both approaches have been blended together with the result that many computations are now performed using a mixture of wavefunction and density approaches within the same computations. This feature brings with it advantages as well as disadvantages. The unfortunate fact is that, as yet, there are no pure density functional methods that are tractable for performing calculations. The philosophical appeal of a universal solution for all the atoms of the periodic system, based on electron density rather than fictitious orbitals, has not yet borne fruit.⁴⁹

CONCLUSION

The aim of this chapter has not been trying to decide whether or not the periodic system is explained by quantum mechanics *tout court*, since the situation is more subtle. It is more a question of the extent of reduction or extent of explanation that has been provided by quantum mechanics.

Whereas most chemists and educators seem to believe that the reduction is complete, perhaps 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, which gathers together a host of empirical data from a level far removed from the microscopic world of quantum mechanics.

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 deductive 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 and that the periodic table will continue to present a test case for the adequacy of new methods developed in quantum chemistry.⁵⁰

Our story has now been brought up to date. From its humble beginnings as a set of isolated triads of elements, the periodic system has grown to embody well more than 100 elements and has survived various discoveries such as that of isotopes and the quantum mechanical revolution in the study of matter. Rather than being swept aside, it has continued to provide a challenge to the development of ever more accurate means of calculating the basic properties of the atoms of the chemical elements. The central role of the periodic system in modern chemistry has been consolidated rather than eroded.

The reduction of chemistry to quantum mechanics has neither failed completely, as some philosophers of science have claimed,⁵¹ nor has it been a complete success, as some contemporary historians have claimed.⁵² The reductive enterprise has been highly successful but not to the extent of deposing the chemical facts or the quintessential discovery of chemical periodicity made by De Chancourtois, Newlands, Odling, Hinrichs, Lothar Meyer, and most significantly, Mendeleev. Rather than undermining chemical periodicity, modern quantum physics has literally re-presented the periodic system and has provided it with a theoretical justification. More important, quantum physics has achieved this feat without assuming the imperialistic role that it is sometimes attributed.