Commentary

How Good Is the Quantum Mechanical Explanation of the Periodic System?

by Eric R. Scerri

The use of quantum mechanics, or more specifically, orbitals and electronic configurations in teaching general chemistry is now such a widespread trend that it would be utterly futile to try to reverse it. Moreover, orbitals and configurations have been extremely useful in providing a theoretical framework for the unification of a multitude of chemical facts.

However, in the course of this brief commentary, I would like to issue a caution regarding the extent to which the periodic table, for example, is truly explained by quantum mechanics so that chemical educators might refrain from overstating the success of this approach. I would also like to raise an issue which, to the best of my knowledge, has only recently been explicitly pointed out in the literature (*1*).

Pauli's explanation for the closing of electron shells is rightly regarded as the high point in the old quantum theory. Many chemistry textbooks take Pauli's introduction of the fourth quantum number, later associated with spin angular momentum, as the foundation of the modern periodic table. Combining this two-valued quantum number with the earlier three quantum numbers and the numerical relationships between them allow one to infer that successive electron shells should contain 2, 8, 18, or $2n^2$ electrons in general, where n denotes the shell number. This explanation may rightly be regarded as being deductive in the sense that it flows directly from the old quantum theory's view of quantum numbers, Pauli's additional postulate of a fourth quantum number, and the fact that no two electrons may share the same four quantum numbers (Pauli's exclusion principle).

However, Pauli's Nobel Prize-winning work did not provide a solution to the question which I shall call the "closing of the periods"—that is why the periods end, in the sense of achieving a full-shell configuration, at atomic numbers 2, 10, 18, 36, 54, and so forth. This is a separate question from the closing of the shells. For example, if the shells were to fill sequentially, Pauli's scheme would predict that the second period should end with element number 28 or nickel, which of course it does not. Now, this feature is important in chemical education since it implies that quantum mechanics cannot strictly predict where chemical properties recur in the periodic table. It would seem that quantum mechanics does not fully explain the single most important aspect of the periodic table as far as general chemistry is concerned.

The discrepancy between the two sequences of numbers representing the closing of shells and the closing of periods occurs, as is well known, due to the fact that the shells are not sequentially filled. Instead, the sequence of filling follows the so-called Madelung rule, whereby the lowest sum of the first two quantum numbers, $n + l$, is preferentially occupied. As the eminent quantum chemist Löwdin (among others) has pointed out, this filling order has never been derived from quantum mechanics (*2*).

Pauli's contribution can only be said to explain the closing of the periods if the correct order of filling is assumed, as indeed it was, in the early electronic versions of the periodic table compiled by Bohr and others. But this order of filling was obtained by reference to experimental facts, especially the spectroscopic characteristics of each of the elements (*3*).

To make matters worse, the Madelung rule shows as many as twenty exceptions, starting with the elements chromium and copper where, although the order of orbital filling is adhered to, the implicit notion that a subshell should be completely filled before proceeding to the next one is violated. As is well known, chromium and copper have electronic configurations involving $4s^1$ configurations rather than the expected $4s^2$. Once again, the "correct" configuration is arrived at not from theory but by reference to the experimental facts. In some of these, the anomalous configuration can be rationalized, again after the facts, by appeal to relativistic effects (*4*), but there is no general explanation for why anomalous configurations occur in the places they do. Yet another blemish in the theoretical aufbau scheme consists of the configurations of elements such as nitrogen and phosphorus where Hund's first rule must be invoked in order to obtain the experimentally correct configurations involving three unpaired p electrons. While acknowledging the work carried out to rationalize Hund's rules in terms of quantum mechanical principles (*5*), this is not the same as strictly deducing the rules from these principles.

Of course, most of what I have said so far is well known. Nevertheless, I hope to have given these issues a new perspective by adopting an almost perversely rigorous approach in demanding that every aspect of electronic configurations should be strictly deducible from quantum mechanics. Although I am not in a position to propose a better explanation, I do not think that we should be complacent about what the present explanation achieves. As I have tried to argue, in terms of deduction from theoretical principles, the present semi-empirical explanation is not fully adequate.

Finally, given that quantum mechanics is here to stay, I would also like to make a plea for presenting chemistry from relativistic quantum mechanics rather than the usually invoked non-relativistic version. Over the past twenty or so years, an increasing number of fairly commonplace chemical phenomena have been explained (admittedly, also after the facts) by detailed calculations that take account of relativistic effects (*6–10*) due to fast-moving, usually inner, electrons. These phenomena include the color of gold (*8*), the saw-toothed patterns seen in the properties of elements in some groups of the periodic table (*6*), the inert-pair effect such as in group IV (*8*), the liquid nature of mercury (*8*), and the anomalous electronic configurations of some elements of the sixth row of the periodic table (*7*).

If we are to take a reductionist approach, then let it be one that is consistent with both of the fundamental theories of physics, the science that chemistry approximately reduces to (*11*).

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