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Perspective

Perspective on "Quantum mechanics of many-electron systems"

Dirac PAM (1929) Proc R Soc Lond Ser A 123: 714

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Abstract. Four prophetic statements in the introductory paragraph of Dirac's probably most cited paper are analyzed. Not only has his claim been disproved that the quantum mechanical equations needed to solve chemical problems are too complicated to ever be solved, even the reduction of chemistry from quantum mechanics is a tricky epistemological problem. Most surprising is that Dirac believed that relativistic effects are unimportant for chemistry.

Key words: Chemical bond – Chemical concepts – Many – electron systems – Reductionism – Relativistic effects

1 Introduction

P.A.M. Dirac, who shared the 1933 Nobel prize for physics with Schrödinger (the 1932 price went to Heisenberg), was one of the greatest pioneers of quantum mechanics. Most of his achievements entered textbooks so fast that his original papers are hardly cited. Nobody, who uses Dirac's bra–ket notation or his "δ function" would cite the original references [1].[1] The same is true of Dirac's time-dependent perturbation theory [2] or of the Dirac equation [3], the basis of relativistic quantum mechanics or of his subsequent work on positrons and holes [4].

There is, however, one paper of Dirac [5] that keeps being cited, namely the one at which we want to have a look now. Most people who cite this paper hardly know that its title is "*Quantum mechanics of many-electron systems*" and are unaware of its scientific context. It deals mainly with the relation between permutation symmetry and spin and contains a formula which relates the expectation value of the operator of electron exchange to the total spin of the state.

$$\langle S^2 \rangle = -\left\langle \sum_{i<j} P_{ij} \right\rangle - \frac{1}{4} n(n-4) \ , \tag{1}$$

where n is the number of electrons and where the sum goes over all distinct exchanges of the spatial coordinates of two electrons.

The popularity of this paper [5] has, however, nothing to do with its scientific content. It is entirely based on the introductory paragraph to be quoted now in full length.

> *The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.*

This introductory paragraph is essentially prophetic, and it is not cited so much because the prophecy has been fulfilled, but rather because it was strongly disproved. The quoted text contains four statements:

1. Relativistic effects are not relevant for chemistry. This claim occupies roughly one half of the introductory paragraph, and apparently the author regarded it as important.
2. A large part of physics and the whole of chemistry can be deduced from quantum mechanics.
3. The equations to be solved for chemical problems are too complicated to be solvable.
4. Approximate practical methods should be developed in order to explain atomic (and probably molecular structure) without too much computation.

We note, by the way, that usually (like recently in the press release of the Nobel committee concerning the 1998 Nobel prize for chemistry) only one sentence of

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[1] These concepts are outlined in Ref. [1], but they may go back to earlier work. In the book no references to original papers are given

the introductory paragraph is quoted, namely the one which contains essentially statements 2 and 3.

Which, if any, of these statements can still be regarded as valid, and what can we learn from their analysis? Let us comment on them in reverse order.

2 Need for simplified methods

Statement 4 was an important guiding principle in the early days of the theory of atomic and molecular structure. Results based entirely on group theory were very helpful. It also turned out to be necessary to formulate approximative theories in terms of empirically adjustable parameters. A nice example of a theory in line with Dirac's suggestion is Slater's theory of complex atoms [6] in which certain parameters F_k or G_k, appeared, that could, in principle, be calculated, but which were rather evaluated from spectral data to get better agreement with experiment. Semiempirical adjustments of theoretical parameters was also essential in Hückel's molecular orbital theory of π-electron systems [7] in order for it to be practically useful. Although the recent developments of ab initio theory make semiempirical parameters obsolete, the trend to oversimplified theories that need to be calibrated by experiment or by benchmark calculations is tending to return, as is demonstrated by the apparent success of modern density functional methods [8, 9].

3 Equations of quantum mechanics are too complicated

When Dirac made statement 3 he could hardly anticipate the spectacular progress in computer technology, without which the verification of statement 2 would hardly have been possible.

Nevertheless the equations to be solved to treat chemical problems by means of the Schrödinger equation are extremely complicated. After all, for an n-electron system one has to solve an eigenvalue problem for a $3n$-dimensional partial differential equation. I still believe that if one asked a competent mathematician, who does not know of the achievements of ab initio quantum chemistry, he would hardly see a chance that these equations could ever be solved, even with modern computers. One should not forget that the very best quantum chemical methods contain serious approximations, often guided by physical or chemical intuition, and that good agreement with experiment is, to a larger extent than is generally admitted, based on a – controlled or fortunate – cancellation of errors. One is also lucky that to answer many chemically relevant questions moderately accurate calculations are sufficient.

While semiempirical methods (including to some extent density functional approaches) rely on adjustable parameters, the quality of the ab initio method could, in principle, be judged by intrinsic criteria. These are, unfortunately, only useful for extremely sophisticated methods applied to very small systems. For the majority of ab initio methods one first checks from the application to known systems how reliable predictions can be expected for unknown ones.

The importance of Boys' ingenious idea [10] to expand wave functions in a Gaussian basis can hardly be overestimated. Gaussian basis functions behave incorrectly near the nuclei and very far from them, but they allow an extremely efficient integral implementation. Only recently has a formal proof been given [11] that an expansion in a Gaussian basis has a satisfactory convergence behavior. Much poorer is the convergence of configuration-interaction-like approaches to treat electron correlation effects [12, 13], but even for this problem progress has been possible recently [14].

4 Can chemistry be derived from quantum mechanics?

When Dirac wrote that "the underlying physical laws are for the whole of chemistry are thus completely" known, this was certainly revolutionary, since it implied that the only forces responsible for chemical phenomena are Coulombic, and that there is no genuine chemical force, as was still widely believed. A few years later Hellmann [15] formulated the program of quantum chemistry "which claims nothing less than to predict all chemical and physical properties of matter purely theoretically based on a simple mathematical law".[2] Some 20 years ago the present author tried to formulate a consistent and rigorous theory of the chemical bond [16] and found that "there is a long way from Dirac's statement (2) to an explicit theory of chemistry on the basis of quantum mechanics". In view of the spectacular success of numerical quantum chemistry that culminated in the Nobel prize for chemistry 1998, there are hardly doubts that at least with statement 2 Dirac was right.

Nevertheless, in his stimulating review, Primas [17] criticizes Dirac as a naive reductionist. According to Primas, Dirac was wrong because his "postulate of reductionism" was based on what Primas calls the "pioneer quantum mechanics" which he contrasted with "modern nonrelativistic quantum mechanics", and that Dirac did not consider the complicated epistemological problems related to the reduction of chemistry from quantum mechanics. It is not the scope of our perspective to comment on this criticism. Note, however, that the two "generations" of quantum theory differ more in the interpretation than in the operative formalism, that was, in fact, fully formulated in 1929. As to the relevance of problems of interpretation for the application of quantum mechanics, the reader is referred to a refreshing paper by Lévy-Leblond [18].

Theory reduction is, in a philosophical sense, certainly not a trivial problem; already the definition of how one understands reduction is crucial. Conclusions on the possibility of theory reduction depend much on this definition. Some scenarios are possible.

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[2] The original quotation is "*Die Quantenchemie maßt sich nicht weniger an als sämtliche chemische und physikalische Materialeigenschaften rein theoretisch vorausberechnen zu können, nur auf Grund eines einzigen mathematischen Gesetzes [... und] die chemische Welt theoretisch nachzukonstruieren*"

1. It may be necessary to amend the underlying theory before the reduction process. In order to derive thermodynamics from classical statistical mechanics, Boltzmann was, for example, obliged to introduce the quasiergodic hypothesis. There are vague speculations that quantum theory may have to be amended for systems with a very large number of particles [17].
2. On the way of reduction, by some limiting process, quantities and concepts may arise that have no place in the underlying theory, such as temperature or entropy or phase transitions as derived from statistical mechanics. The appearance of macroscopic irreversibility from microscopic irreversibility is still a controversial topic.
3. Finally reductionism may fail, i.e. it may not be possible to derive essential concepts of a "subtheory" from a supertheory. There is no evidence that this might be the case for the reduction of chemistry from quantum mechanics. The most challenging candidate for such a new concept is "life", which arises when one goes one step further down in Comte's [19] hierarchy of sciences, namely to biology.

The best understood examples of theory reduction are those of classical mechanics from quantum mechanics and thermodynamics from quantum statistics. Both classical mechanics and statistical mechanics can be either formulated by theory reduction or directly in terms of intrinsic axiomatics without reference to the underlying higher level theory. They have a different logical structure than quantum mechanics, for example, all variables commute.

In addition to quantum chemistry, which is a theory at a microscopic scale, there is place for macroscopic chemical theories such as chemical thermodynamics. In this context the reformulation of electrochemistry by Hertz [20] also deserves attention. On the other hand, many "prequantum" theories of the chemical bond had to be abandoned, because they turned out to be inconsistent with quantum chemistry. The "theory of mesomerism" survived for a while because it was regarded as a mapping to a simplified quantum chemical model, that of the semiempirical valence-bond theory, until both the former and the latter became obsolete.

There is certainly a challenge for genuine chemical theories, but there appears to be agreement that they have to conform with molecular quantum mechanics.

Typical chemical concepts are not as sharp as typical physical concepts. A nice example is that of atomic charge densities which were analyzed [21] in terms of "factor analysis" and were found to be "scalar" quantities (different possible definitions do not lead to the same numerical values, but these correlate satisfactorily), at variance with "aromaticity" [22, 23] which turned out to be a "multidimensional half-ordered" concept [23]. Primas [17] suggested that "molecular structure" is a genuine chemical concept, which has no counterpart in rigorous quantum mechanics. On the other hand, situations where molecular structures become undefined do show up in chemistry, or at least in molecular spectroscopy. Quantum phenomena apparently have a stronger tendency to survive in chemistry than in macroscopic physics. After all, the chemical bond can only be understood in terms of quantum mechanics [16, 24–26].

A useful theory reduction generates convenient intermediate levels. In order to understand the three-dimensional structure of proteins one will certainly not go back to the Schrödinger equation for the protein, but to a force-field model, that by itself is derivable – at least in principle – from quantum mechanics.

Whether a mathematical formulation of chemistry (as is now familiar to us) is possible or even desirable has been a controversial subject over the centuries. In 1786 Kant wrote [27] that chemistry will never be a genuine science because it cannot be formulated in mathematical terms.[3] While Gay-Lussac [28] believed in 1808 that in the near future the majority of chemical phenomena will be calculable, Comte [19] in 1830 even went beyond Kant and claimed that mathematics and chemistry are mutually exclusive, and that a – fortunately unlikely – mathematical access to chemistry would imply its decline.[4]

More recently Wigner argued that even if we were able to solve the Schrödinger equation numerically to any desired accuracy, this would not provide physical insight [29]. Wigner's view of physical insight is very puristic. What one cannot verify on the back of an envelope is, in his view, no acceptable theory. This opinion is to some extent shared by Longuet-Higgins [30], who has proposed to divide chemists into three classes: experimentalists, computationalists and theorists. In his opinion – and to some extent that of Primas [17] – computational chemistry is not theory. Future generations will probably have difficulties to understand the somewhat irrational aversion of some scientists of the twentieth century to insight obtained by means of computer application, although of course use of computers should not replace thinking.

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[3] The original quotation is
Solange als noch für die chymischen Wirkungen der Materien aufeinander kein Begriff ausgefunden wird, der sich construieren läßt, d. i. kein Gesetz der Annäherung oder Entfernung der Theile angeben läßt, nach welchem etwa in Propertionen ihrer Dichtigkeiten u. d. g. ihre Bewegungen samt ihren Folgen sich im Raume a priori anschaulich machen und darstellen lassen (eine Forderung, die schwerlich jemals erfüllt werden wird), so kann Chymie nichts mehr als systematische Kunst, oder Experimentallehre, niemals aber eigentliche Wissenschaft werden, weil die Principien derselben blos empirisch sind und keine Darstellung a priori in der Anschauung erlauben, folglich die Grundsätze chymischer Erscheinungen ihrer Möglichkeit nach nicht im mindesten begreiflich machen, weil sie der Anwendung der Mathematik unfähig wird

[4] The original quotation is
Toute tentative de faire rentrer les questions chimiques dans le domaine des doctrines mathémathiques doit être réputée jusqu'ici, et sans doute à jamais, profondément irrationnelle, comme étant antipathique à la nature des phénomènes... si, par une aberration heureusement presque impossible, l'emploi de l'analyse mathématique acquérait jamais, en chimie, une semblable prépondérance, il déterminerait inévitablement, et sans aucune compensation, dans l'économie entière de cette science, une immense et rapide rétrogradation, en substituant l'empire des conceptions vagues à celui des notions positives, et un facile verbiage algébrique à une laborieuse exploration des faits

5 Are relativistic effects unimportant for chemistry?

Dirac's statement 1 is most surprising, if one realizes that he was the very one who formulated in an ingenious way the relativistic theory of an electron [3]. He did not say explicitly why he thought that relativistic effects were negligible in atomic or molecular theory, but apparently he had an argument in mind that was still popular some 50 years later. It is undeniable that relativity affects the motion of electrons if their speed is of the order of magnitude of the velocity of light, and this is the case for the K-shell electrons in heavy atoms. It was argued that chemical bonding only involves the valence electrons, which "move slowly", and that the inner shells are not affected by bonding, such that their relativistic effects cancel in binding energies or other valence-shell problems. It took a long time until it was found that this argument is invalid. The inner shells do affect the valence shell in two ways:

1. By the requirement of orthogonality, which affects mainly valence orbitals with low angular momentum quantum number (in a classical picture the corresponding orbits penetrate into the core region).
2. By a screening of the nuclear charge which is different from that in the nonrelativistic situation.

On the whole valence orbitals of *s*- and *p*-type are shrunk, *d*- and *f*-type orbitals expanded. Although we know that electron spin is not a relativistic effect, since a formulation of nonrelativistic quantum mechanics is possible in which the electron spin appears naturally [31], spin–orbit interaction definitely has a relativistic origin, and is actually the most important relativistic effect. It leads, for example, to a splitting of *p* atomic orbitals into $p_{1/2}$ and $p_{3/2}$ orbitals, which not only have different energy, but also different radial extension. Relativistic effects on the energy are generally of the order $O(Z^2\alpha^2)$ relative to the nonrelativistic energies, where Z is the nuclear charge and α is about 1/137, the fine-structure constant. The fact that relativity mainly affects the inner electrons, was for a long time interpreted in the sense that relativistic effects for different shells in an atom scale as approximately $Z_{\mathrm{eff}}^2\alpha^2$, with the effective charge Z_{eff} for the valence shell differing rather little in one column of the periodic table. In reality there is a dependence of approximately $Z^2\alpha^2$ with the full Z even for valence electrons.

The importance of relativistic effects on chemistry has been reviewed, for example, by Pyykkö [32]. We just mention that gold is regarded as the most relativistic element and that its chemistry is largely determined by relativistic effects, even its colour, as well as the low boiling point of mercury. Many examples on relativistic effects on bond length are known [32], but relativity also affects the overall structure of molecules [33]. Relativistic effects are not limited to heavy atoms, even the reaction $H_2 + F \rightarrow HF + H$ cannot be described quantitatively if one ignores spin–orbit coupling [34]. Let us mention finally that, in spite of its uncontested validity, there are mathematical problems with the Dirac equation [36]. Moreover it is a one-electron equation, the generalization of which to *n*-electron systems is by no means trivial, but available approximate relativistic Hamiltonians appear to work.

6 Conclusions

1. Controversial papers are cited more frequently than uncontested ones, especially so long after their publication [35].
2. Scientific progress consists largely of disproving authoritative statements. There is hardly a better challenge to do something than a claim by someone like Dirac that it is impossible.
3. The question to what extent chemistry is reducible from quantum mechanics is still a nontrivial philosophical problem.
4. Applied quantum mechanics will continue to be an important tool in chemistry. There is still need for methodological advances.
5. Dirac cannot be blamed for his belief that the practical use of quantum mechanics for chemistry will never come; however, he should have realized that relativistic effects are important in chemistry.

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