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# Chemists Without Knowing It? Computational Chemistry and the Møller-Plesset Perturbation Theory

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**Abstract.** This paper considers aspects of the chemistry-physics relationship from a historical perspective and with a focus on the entrance of quantum mechanics in twentieth-century chemistry. Traditionally, theoretical physics was widely regarded as epistemically superior to chemistry if also, from the chemists' point of view, of little practical relevance. With the emergence of quantum chemistry in about 1930, the gulf widened as it seemed that the new discipline was more physics than chemistry. One way of investigating theoretically many-electron atoms was by means of the Hartree-Fock approximation method. The Møller-Plesset perturbation theory introduced in 1934 by a Danish and an American physicist was a refinement to the Hartree-Fock method. Although the Møller-Plesset theory was initially neglected – and is still neglected in the historiography of quantum chemistry – it came to play a most important role in later studies. Indeed, it is a prime example of what in sociological studies of science is known as a “sleeping beauty.” The paper discusses the historical context of the Møller-Plesset theory, concluding that, in a sense, its originators were “chemists without knowing it.”

**Keywords:** quantum chemistry, chemistry-physics relations, Møller-Plesset theory, chemistry Nobel Prizes, sleeping beauties.

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## 1. INTRODUCTION

Much has been written on the physics-chemistry relationship from both a historical and philosophical perspective.<sup>[1]</sup> In the first part of this paper I briefly discuss how physicists have often considered chemistry a science inferior to their own (Section 2). This somewhat condescending attitude was only reinforced with the advent of the so-called old quantum theory principally due to Niels Bohr and Arnold Sommerfeld (Section 3). The second part is devoted to the emergence and early development of quantum chemistry based on post-1925 quantum mechanics (sections 4-5). Rather than dealing with the chemical bond, a classical and well-researched area of the quantum-chemical revolution, the paper looks at a theory of many-electron systems from 1934 which seems to have been forgotten in the historical literature

(Section 6). This theory, the Møller-Plesset perturbation theory or method, has an interesting and little-known history. It illustrates in its own way how physicists unintentionally could make important contributions to theoretical chemistry. Moreover, it also illustrates the concept of a “sleeping beauty,” a term used for scientific papers which hibernate for a long time until they are called alive and become highly influential (Section 7). In the final Section 8 I briefly reconsider the physics-chemistry relationship in the light of the history of the Nobel prizes awarded to either physicists or chemists.

## 2. CHEMISTRY VERSUS PHYSICS? THE EARLY PHASE

The relationship between the two sister sciences chemistry and physics has never been fixed but always in a state of flux. Traditionally, physics was considered the big brother, a much nobler and more scientific field than the supposedly primitive and empirical chemistry. This is an old image still widely shared in the public and also, regrettably, by many scientists. As far back as 1669 Bernard Fontenelle, the perpetual secretary of the Académie Royale des Sciences in Paris, wrote as follows:

*Through its visible operations, chemistry resolves bodies into a certain number of crude tangible principles; salts, sulfurs, etc. while through its delicate speculations, physics acts on the principles as chemistry acts on bodies, resolving them into other even simpler principles, small bodies fashioned and moved in an infinite number of ways. ... The spirit of physics is clearer, simpler, less obstructed, and, finally, goes right to the origins of things, while the spirit of chemistry does not go to the end.<sup>[2]</sup>*

More than a century later, after Newton's mechanical physics had been generally accepted, Immanuel Kant repeated Fontenelle's message of chemistry's lower epistemic status. Not only was chemistry inferior to Newtonian physics, according to Kant it was not even a genuine science and could never become one. The problem was that by its very nature laboratory-based chemistry was, or was claimed to be, intractable to the mathematical method and systematic deduction from higher laws or principles. As Kant expressed it in his *Metaphysische Anfangsgründe der Naturwissenschaft* from 1786:

*Chemistry can be nothing more than a systematic art or experimental doctrine, but never a proper science, because its principles are merely empirical, and allow of no a priori presentation in intuition. Consequently, they do not in the least make the principles of chemical appearances conceivable with respect to their possibility, for they are not receptive to the application of mathematics.<sup>[3]</sup>*

At the time when Kant degraded chemistry to a non-science there were already a few attempts to apply mechanical physics to chemical phenomena, indeed to subjugate the latter under the former. Thus, in an ambitious work of 1758 with the characteristic title *Essai de Chymie Mécanique* the Swiss natural philosopher Georges-Louis Le Sage claimed to have explained chemical affinity and properties of matter purely in terms of mechanical physics. According to Le Sage, cohesion, affinity, and gravitation were all aspects of the same general law of mechanics.<sup>[4]</sup>

Later in the century, the Newtonian paradigm came to be highly regarded by chemists and physicists in the French tradition mainly due to Pierre-Simon Laplace and Claude Louis Berthollet. However, the dream of a Newtonian chemistry was more rhetoric than reality. It remained a dream and in the early part of the nineteenth century it was realized to be a dead end.<sup>[5]</sup> During the last quarter of the century the dream was shortly revived in the version of “vortex chemistry” based on the mathematically advanced theory of the vortex atom proposed by William Thomson, J. J. Thomson, William Hicks, and other British physicists. However, to the large majority of chemists this theory was too much physics and mathematics, and too little chemistry. Latest by the turn of the century vortex chemistry (and vortex atom theory generally) was abandoned.<sup>[6]</sup> Still, a few chemists in Britain and the United States responded favorably to J. J. Thomson's vision of a vortex chemistry. Harry C. Jones, a physical chemist at Johns Hopkins, referred positively to the theory in a textbook of 1902. And according to Francis Venable, professor of chemistry at the University of North Carolina, the vortex theory of matter offered a future theory of everything which included all chemical phenomena.<sup>[7]</sup>

When speaking about the chemistry-physics relationship over long periods of time it is important to avoid anachronisms and keep in mind that the terms “chemistry” and “physics” once had different meanings than they have today. What Fontenelle and Kant referred to with these terms cannot be directly translated into the sciences as known in the second half of the nineteenth century. This said, we shall first briefly consider some aspects of the relationship between chemistry and physics in the period from about 1880 and 1920. By that time Kant's claim of chemistry as a non-scientific art had long been contradicted by its explosive development. And yet the epistemic status of chemistry as compared to that of physics remained a matter of discussion.

With the emergence of chemical thermodynamics, a highly abstract yet empirically powerful theory developed principally by Josiah Willard Gibbs in the United

States and Hermann Helmholtz in Germany, it seemed for a while that chemistry had been solidly founded in universal laws of nature. However, it was a foundation laid by physicists with no experience in laboratory chemistry and no high opinion of the kind of work most chemists were engaged in. As Helmholtz arrogantly expressed it in a letter of 1891: “Thermodynamic laws in their abstract form can only be grasped by rigorously schooled mathematicians, and are accordingly scarcely accessible to the people who want to do experiments on solutions and their vapor tensions, freezing points, heats of solution, &c.”<sup>[8]</sup> Helmholtz referred somewhat condescendingly to the new school of physical chemistry established by Svante Arrhenius, Jacobus van’ t Hoff, Wilhelm Ostwald, and others.

Nevertheless, by the turn of the century a small group of chemists had become “rigorously schooled mathematicians” who mastered the abstract theory of thermodynamics. One of them was the Dutch chemist Johannes van Laar who in a series of works cultivated thermodynamics as the royal road to what he called “mathematical chemistry.”<sup>[9]</sup> On the other hand, although thermodynamics was a major step toward integrating physics and chemistry, it was at most a partial integration. After all, thermodynamics is concerned only with the state functions and bulk matter, whereas it is not applicable to the chemical elements and compounds – or to atoms and molecules – that chemistry is first and foremost about.

Traditional chemists found the mathematics of physical theories to be incomprehensible as well as irrelevant for their science, and there were also other reasons why many of them resisted what they felt was an intrusion of physics into chemistry. One of the reasons was the discovery in the 1890s of radioactivity and the electron. The great Dmitri Mendeleev was in some respects a traditionalist who firmly believed that if the physicists’ subatomic particle (the electron) and transmutation of elements (radioactivity) were accepted, chemistry would degrade into a pre-scientific state.<sup>[10]</sup> He thought to have found an alternative to the new physics in the form of the ether, which he, contrary to the physicists, conceived as an ultralight chemical element with a place in the periodic table. Referring to radioactivity and what he called the “metachemical” electron, he stated: “It is my desire to replace such vague ideas by a more real notion of the chemical nature of the ether.”<sup>[11]</sup> Mendeleev wanted to establish the supremacy of chemistry over the new physics, but the large majority of scientists – whether physicists or chemists – ignored his grand project.

Although Mendeleev’s proposal of incorporating the world ether as an essential part of chemistry failed,

several contemporary chemists shared his skeptical or even hostile attitude to the new physics. One example is Arthur Smithells, professor of chemistry at the University of Leeds, who in a presidential address to the 1907 meeting in Leicester of the British Association for the Advancement of Science (BAAS) warned against what he called the “invasion” of chemistry by mathematics and physics:

*With radioactivity, in relation to the ponderable, we seem almost to be creating a chemistry of phantoms ... associated as it is with the exuberance of mathematical speculation of the most bewildering kind concerning the nature, or perhaps I should say the want of nature, of matter. ... Though chemistry and physics meet and blend there is an essential difference between the genius of physics and the genius of chemistry. Apart from his manipulative skills, the latter is not given to elaborate theories and is usually averse to speculation; nor has he the usually an aptitude in mathematics. ... Chemistry should not be invaded by mathematical theorists.*<sup>[12]</sup>

Henry Armstrong, like Smithells a chemical traditionalist, noted in another presidential address to the chemical section of BAAS two years later that “now that physicists are regular excursionists into our territory, it is essential that our methods and our criteria be understood by them.” He found it “a serious matter that chemistry should be so neglected by physicists.”<sup>[13]</sup>

### 3. QUANTUM THEORY ENTERS CHEMISTRY

The gulf between chemistry and physics only deepened with the advent of Niels Bohr’s quantum atom which not only addressed physical problems but also chemical. After all, the title of his three seminal articles in the 1913 volume of *Philosophical Magazine* was “On the Constitution of Atoms and Molecules.” Bohr applied the new theory to problems which traditionally belonged to chemistry, such as the heat of formation of molecular hydrogen, the covalent bond, and the periodic system of the elements.<sup>[14]</sup> In an address of 1920 given to the Royal Danish Academy of Sciences, he cautiously suggested that in the future theoretical chemistry might become a branch of atomic physics: “Since ... a possibility has been opened up of interpreting chemical experiences with the aid of considerations originating in the so-called physical phenomena, a connection between physics and chemistry has been created which does not correspond to anything conceived of before.”<sup>[15]</sup>

Other theoretical physicists were more direct in their reductionist attitude to the physics-chemistry relationship. Max Born in Göttingen tended to see chemis-

try as inferior to physics because chemistry – which he, contrary to Kant, after all admitted as a proper science – lacked a mathematical foundation. To illustrate his point, he made use of a military metaphor:

*We realize that we have not yet penetrated far into the vast territory of chemistry, yet we have travelled far enough to see before us in the distance the passes that must be traversed before physics can impose her laws upon her neighbor science.*<sup>[16]</sup>

For a while, several physicists thought that Bohr, with his new quantum theory of atoms and molecules, might become the new Newton who succeeded in basing chemistry deductively on the higher principles of physics. The British physicist Oliver Lodge referred implicitly to the Kantian dream of a mathematized chemistry when he lyrically wrote about “The brilliant attempts at further analysis of the atoms of all the chemical elements, so as to deduce their properties – the full beauty of atomic astronomy which is now unfolding before the eyes of enthusiastic experts.” He concluded that, “we are living in the dawn of a kind of atomic astronomy which looks as if it were going to do for Chemistry what Newton did for the Solar System.”<sup>[17]</sup> Born’s colleague in Göttingen, the great mathematician David Hilbert, was more explicit. According to him, the desired reduction of chemistry to physics required “a Newton of atomic theory, and this has been Niels Bohr, who on the basis of new physical ideas, namely, the quantum theory, made a deeper understanding of this area a possibility.”<sup>[18]</sup>

However, not everyone, and as expected not the chemists in particular, agreed that Bohr was a new Newton or, for that matter, that chemistry needed to comply with the strange laws of quantum physics. In fact, Bohr’s attempt to extend the quantum theory of atomic structure to the realm of chemistry was considered unconvincing by most chemists. Their dissatisfaction with the semi-classical Bohr atom was given voice by the American physical chemist Richard Tolman, who, contrary to many of his colleagues in the chemical sciences, was also an accomplished mathematician. In an address delivered in Toronto in 1921, he objected to Bohr’s postulates of stationary states and the mechanism of light emission in terms of quantum jumps. With respect to the Bohr-Sommerfeld atom he said that it was “constructed by the physicists, like a solar system ... partly because they were entirely unfamiliar with the actual facts concerning the behavior of atoms in chemical combination.”<sup>[19]</sup> Moreover, pretending to represent the average chemist, he stated the chemist’s point of view as

*... extreme hostility to the physicists, with their absurd atom, like a pan-cake of rotating electrons, an attitude which is only slightly modified by a pious wish that somehow the vitamin “h” [Planck’s constant] ought to find its way into the vital organs of their own, entirely satisfactory cubical atom. ... In general I feel that the cubical atom of Lewis and Langmuir must be regarded as representing chemical facts better than anything proposed by the physicists.*

Without going into further detail, molecular structure remained an unsolved problem within the framework of the old quantum theory which was unable to explain even the simplest molecules such as H<sub>2</sub> and H<sub>2</sub>. The result was that the majority of chemists disregarded the Bohr-Sommerfeld theory and instead adopted the “cubical atom” with fixed electrons such as proposed by Gilbert N. Lewis and Irving Langmuir in particular. Although this kind of atomic model was pure nonsense according to the quantum physicists, from the point of view of the chemists it was useful and of great heuristic value.<sup>[20]</sup> The objections of the physicists were summarized by Edward Andrade, professor of physics at the Artillery College, Woolwich, who wrote about Langmuir’s model of the atom: “It is scarcely necessary to insist on the artificiality of this picture... The electrons in Langmuir’s atom have, in fact, so few of the known properties of electrons that it is not immediately clear why they are called electrons at all.”<sup>[21]</sup>

#### 4. THE EMERGENCE OF QUANTUM CHEMISTRY

Chemical considerations played no role in the establishment of quantum mechanics as the theory was formulated 1925-1926 principally by Heisenberg, Born, and Jordan (matrix mechanics), Dirac (q-number algebra), and Schrödinger (wave mechanics).

As seen in retrospect, modern quantum chemistry took its beginning with a seminal paper of 1927 written by two German physicists, 27-year-old Fritz London and the four years younger Walter Heitler. The title of their paper in *Zeitschrift für Physik* was “Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik” (The Interaction of Neutral Atoms and Homopolar Bond According to Quantum Mechanics).<sup>[22]</sup> The basic approach of the Heitler-London theory of the H<sub>2</sub> molecule was to consider separately one of the electrons in each of the combining atoms and then, by means of approximation methods and taking into regard the recently discovered resonance effect, to construct a wave function representing the paired-electron bond between them. Apart

from explaining the formation of  $H_2$  from two hydrogen atoms, they also explained why two helium atoms cannot form a  $He_2$  molecule. Without making use of any empirical data, Heitler and London estimated from their *ab initio* calculations the dissociation energy of the molecule to be about 2.4 eV.

In a more general sense the main result of the Heitler-London paper was its deductive argument that the covalent bond can be explained purely in terms of spin quantum mechanics and is therefore outside the reach of classical chemistry. The pioneering work of the two physicists suggested a mathematization of chemistry more real and thorough than what had previously been dreamt of. It can be regarded as yet another example of the “invasion” of a chemical territory by theoretical physicists with basically no background in or knowledge of laboratory chemistry. In a letter to Heitler from 1935, London indicated his lack of respect for the culture of chemistry:

*The word “valence” means for the chemist something more than simply forces of molecular formation. For him it means a substitute for these forces whose aim is to free him from the necessity to proceed, in complicated cases, by calculations deep into the model. ... The chemist is made out of hard wood and he needs to have rules even if they are incomprehensible.*<sup>[23]</sup>

Given Linus Pauling’s background in chemistry and later reputation as a “chemical translator,” it is noteworthy that in his younger days he subscribed to the reductionist view expressed by some quantum theorists. Thus, in a lecture from 1928 to the American Chemical Society, he stated that chemistry was a kind of by-product of theoretical physics:

*We can now predict with a considerable measure of confidence the general nature of the future advances [in theoretical chemistry]. We can say, and partially vindicate the assertion, that the whole of chemistry depends essentially upon two fundamental phenomena: these are (1) the one described in the Pauli Exclusion Principle; and (2) the Heisenberg-Dirac Resonance Phenomenon.*<sup>[24]</sup>

Pauling’s assertion had more than a little in common with Dirac’s better-known claim from the following year (see below).

The approach of Heitler and London formed the backbone of what came to be known as the valence bond (VB) method, which in the version developed by Pauling and others dominated quantum chemistry during the 1930s. The alternative molecular orbital (MO) method can be traced back to a paper that yet another German physicist, Friedrich Hund, published in 1927.

Hund assumed that an individual electron moved in the field from all the nuclei and the other electrons in the molecule. His approach was paralleled by works done by Robert Mulliken, who contrary to Hund had a solid chemical training and a PhD in physical chemistry. At around 1931 the two methods, valence bond and molecular orbitals, reached immaturity and quantum chemistry entered as a social and scientific reality.

The concept of “chemical physics” was well known in the nineteenth century, when it typically referred to chemical agents such as heat, light, and electricity.<sup>[25]</sup> It now re-emerged in a different form which indicated the growing autonomy of quantum chemistry. The *Journal of Chemical Physics* was founded in 1933 with Harold Urey as its first managing editor. In the first issue Urey reflected on the old theme of the relationship between physics and chemistry, which he thought had entered a new and fruitful phase of symbiotic cooperation:

*At present the boundary between the sciences of physics and chemistry has been completely bridged. Men who must be classified as physicists on the basis of training and of relations to departments or institutes of physics are working on the traditional problems of chemistry; and others who must be regarded as chemists on similar grounds are working in fields which must be regarded as physics.*<sup>[26]</sup>

The new journal was aimed for contributions too mathematical for *Journal of Physical Chemistry*, too physical for *Journal of the American Chemical Society*, and too chemical for *Physical Review*. Although it contained many articles on quantum chemistry, *Journal of Chemical Physics* was not devoted to this branch of science. As many or more articles were on molecular spectroscopy, kinetics of reactions, materials science, and more traditional areas of physical chemistry. Only in 1967 did the community of quantum chemists get its own journal, the *International Journal of Quantum Chemistry* created by Per-Olov Löwdin, the influential Swedish expert and a major force in establishing quantum chemistry as a proper scientific discipline.<sup>[27]</sup>

Most but not all of the post-World War II generation of chemists came to realize that theoretical chemistry is essentially based on the laws of quantum mechanics. “The whole of chemistry is one huge manifestation of quantum phenomena,” wrote Carl Johan Ballhausen, a professor of chemistry at the University of Copenhagen best known for his important contributions to so-called ligand field theory. According to Ballhausen:

*Without a background in quantum theory it is impossible to possess an “in depth” understanding of chemistry. The elucidation of chemical phenomena by means of the quan-*

*tum laws is now left to the chemists; the solid state physicists do not have the necessary chemical background and the high energy physicists are not interested in electrons. Let us therefore think in deep gratitude and admiration to those pioneering physicists who opened the doors to modern chemistry.*<sup>[28]</sup>

Ballhausen and his contemporaries had no problem with recognizing quantum chemistry as based on work done by physicists and only subsequently developed by chemists.

## 5. EARLY MANY-ELECTRON THEORIES

Although not originally recognized to belong to the domain of quantum chemistry, in the years around 1930 several physicists dealt with the problem of calculating systems with many electrons. One of them was Paul Dirac, who in a paper of 1929 studied the exchange interaction of several identical particles such as electrons belonging to the same atom. When Dirac's paper is still cited today it is not so much because of its scientific content but rather because of its introductory remarks concerning the hypothetical reduction of chemistry to physics:

*The general theory of quantum mechanics is now almost complete ... 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.*<sup>[29]</sup>

Dirac referred in his paper not only to the Heitler-London theory but also to an important theory by the Cambridge mathematical physicist Douglas R. Hartree, who in a series of papers published 1928-1929 in the *Proceedings of the Cambridge Philosophical Society* introduced the so-called self-consistent field approximation method for calculation of many-electron atoms.<sup>[30]</sup> The general idea of this method was to reduce the many-electron problem to a one-electron problem, which was done by representing the effect of an electron on other electrons by a sort of average field corresponding to a central non-Coulomb field of force. In this way Hartree could obtain an approximate solution to the Schrödinger equation even for fairly complicated atomic systems (such as Na<sup>+</sup> and Cl<sup>-</sup>) that agreed well with observed values.

However, as was realized early on by John Slater and a few other physicists, the Hartree method was in some

respects flawed as it disregarded the spin states and the associated Pauli exclusion principle.<sup>[31]</sup> In 1930 the Russian physicist Vladimir Fock published a mathematically complex paper in *Zeitschrift für Physik* in which he improved the method by taking into consideration that the indistinguishability of electrons give rise to exchange forces.<sup>[32]</sup> The result was what soon became known as the Hartree-Fock approximation method, which since then has played an important role in quantum-chemical calculations. However, initially the method was applied exclusively to small and medium-sized atoms, and even in these cases calculations based on the Hartree-Fock theory were laborious. To extend the method to molecules required computational resources that were available only in the post-World War II era.

Whereas the papers of Hartree and Fock attracted critical interest among physicists, as indicated by citations to them they were largely ignored by the chemists. Thus, during the period 1928-1932 Hartree's first paper on the self-consistent field method received 27 citations, all of them in *Physical Review* or other physics journals (Google Scholar). The picture is the same with Fock's paper, which during 1930-1934 was cited 9 times. There were no citations to either of the papers in journals of chemistry or physical chemistry.

The Hartree-Fock method was not the only approach to many-electron calculations developed in the 1930s. In calculations based on this method, the interaction between electrons of opposite spins was taken into account only by means of an average interaction. To remedy for this deficiency various so-called electron correlation methods were developed, the first and arguably most important of which was the Møller-Plesset perturbation theory dating from 1934. According to a review paper of 2011:

*In 1934, Møller and Plesset described in a short note of just five pages how the Hartree-Fock (HF) method can be corrected for electron pair correlation by using second-order perturbation theory. This approach is known today as Møller-Plesset perturbation theory, abbreviated as MPPT or just MP in the literature. MPPT, although in the beginning largely ignored, had a strong impact on the development of quantum chemical ab initio methods in the past 40 years.*<sup>[33]</sup>

Although thousands of papers have been written on this widely used perturbation method, many of them referring to the original paper from 1934, it and its two authors are nearly invisible in the historical literature on quantum and computational chemistry.<sup>[34]</sup> Most likely, very few of the modern scientists using the method and referring to the 1934 paper have any idea of whom

Møller and Plesset were. So, who were they and what was the context of their contribution to what retrospectively can be identified as the history of quantum chemistry? If the Møller-Plesset theory had a strong impact only from about 1970, what about the earlier history?

## 6. MØLLER-PLESSET THEORY IN THE 1930S

As Christian Møller and Milton Plesset stated in their abstract, “A perturbation theory is developed for treating a system of  $n$  electrons in which the Hartree-Fock solution appears as the zero-order approximation.” And later in the paper: “Thus, the perturbation method shows that the theory of the self-consistent field is accurate in the determination of energy to the second approximation.”<sup>[35]</sup> In other words, Møller and Plesset used the Hartree-Fock theory as a starting point but added a small perturbation given by the deviation of the Hartree-Fock Hamiltonian (energy operator) from the exact Hamiltonian. The perturbation term of the second order corresponded to the electron-electron interaction neglected in the Hartree-Fock theory.

Møller is described in a Wikipedia article on him as “a Danish chemist and physicist,” which is a gross mistake given that neither he nor his coauthor Plesset ever worked in or published on chemistry.<sup>[36]</sup> They were quantum physicists with no interest whatsoever in chemistry or even recognizing that their short paper in *Physical Review* belonged to the new fields of chemical physics and quantum chemistry. The two authors did not offer any application or calculation, as for instance Hartree did. They considered their work to be a contribution to theoretical quantum mechanics and no more than that. In fact, the words “atom” and “molecule” did not appear in the article, which also did not mention “chemistry” or related terms. Nor did it refer to experimental data of any kind.

Christian Møller (1904-1980) was a 30-year-old Danish physicist at Bohr’s institute of theoretical physics in Copenhagen (Figure 1). At the time he was best known for an important quantum theory of relativistic electron-electron scattering, a phenomenon which became known as Møller scattering.<sup>[37]</sup> By 1934, when he collaborated with Plesset, he had begun working on Enrico Fermi’s new theory of beta-radioactivity. Shortly after having completed the paper with Plesset, he went to Rome on a Rockefeller stipend to work with Fermi’s group. Later in his career Møller turned to the meson theory of nuclear forces, to which he contributed with several papers in the period from 1939 to 1946. In 1943 he was appointed professor of mathematical physics



Figure 1. Portrait photograph of Christian Møller, 1936. Credit: Niels Bohr Archive, Photo Collection, Copenhagen.

at the University of Copenhagen. Since the early 1950s Møller focused increasingly on the theory of general relativity on which subject he became internationally recognized as a leading expert. His authoritative and much-used textbook from 1952 titled *The Theory of Relativity* played an important role in the so-called renaissance of general relativity.

Milton Spinoza Plesset (1908-1991) earned his PhD at Yale University in 1932 and subsequently moved to Caltech, where he worked with J. Robert Oppenheimer on positron theory and problems of quantum electrodynamics. In 1933 he went to Bohr’s institute in Copenhagen on a National Research Council fellowship. In September that year he participated in the annual institute conference with, among others, Møller, Dirac, Heisenberg, and Heitler (Figure 2). While in Copenhagen he also accompanied Bohr and his wife on a visit to the Soviet Union in May 1934, where he met Fock and other Russian physicists. And then he found time to collaborate with Møller on the many-electron theory which came to bear their names.



**Figure 2.** Conference at Bohr's institute, September 1933. On the first row: N. Bohr, P. Dirac, W. Heisenberg, P. Ehrenfest, M. Delbrück, L. Meitner. Milton Plesset is on the second row, number four from the right, and Christian Møller seats behind him, number three from the right on the third row. Credit: Niels Bohr Archive, Photo Collection, Copenhagen.

Bohr valued Plesset as a very promising physicist, such as evidenced in a letter he wrote to an American colleague:

*Surely he is one of the best of young American theoretical physicists and especially he has as you know a great insight in the relativistic quantum theory of the electron... He hopes soon to publish an account of some of his work together with [John] Wheeler, and you may perhaps have seen a recent paper in the Physical Review on the many-electron problem, which he published a few months ago together with Møller.<sup>[38]</sup>*

After having worked in Copenhagen and elsewhere in Europe, Plesset returned to Caltech where he was appointed professor in engineering science in 1963. His scientific work after World War II was mostly concerned with fluid dynamics and nuclear physics (Figure 3).<sup>[39]</sup>

The paper by Møller and Plesset was predominantly mathematical, with no indication at all of the areas of physics and chemistry to which the theory might be applied. Apparently they did not care. None of the two Copenhagen physicists considered their work to be important and they never returned to it or related fields of science. When Plesset was interviewed in 1981, he did not even mention Møller and the work he did with him.<sup>[40]</sup>

As shown by the number of citations to the 1934 paper, for a long period the Møller-Plesset theory was ignored. During the 1930s the paper received only 5 citations, all of them in *Physical Review* except one in *Journal de Physique et le Radium* written by the Swedish theoretical physicist Oskar Klein. While two of



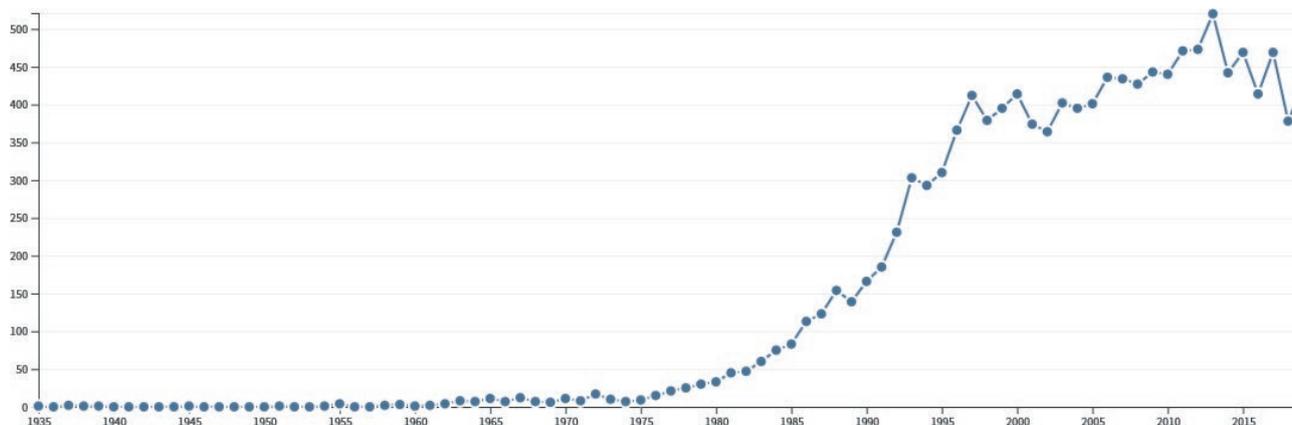
**Figure 3.** Milton Plesset (left) with N. Bohr, F. Kalckar, E. Teller, and O. Frisch at the Copenhagen institute in 1934. Credit: Niels Bohr Archive, Photo Collection, Copenhagen.

the citing papers considered the theory in relation to nuclear structure, none of them referred to the electron structure of atoms. By 1962 the cumulative number had increased to 22, less than one citation per year in average. In other words, the Møller-Plesset perturbation method was scarcely visible in the scientific literature. However, the poor record changed drastically from about 1980 – the year that Møller died – and today the total number of citations to the Møller-Plesset paper has exploded to about 16,600 according to Google Scholar or 13,600 according to Web of Science (Figure 4). Of course, when evaluating such citation curves one has to take into consideration the general growth in the numbers of publications in the period.<sup>[41]</sup> But even then the Møller-Plesset citation curve is highly anomalous.

## 7. A SLEEPING BEAUTY

The fate of the Møller-Plesset theory only changed when computers began to be widely used to solve problems in chemical physics and quantum chemistry. According to Dieter Cremer, a German specialist in computational chemistry, perturbation theory as a tool in theoretical chemistry was rediscovered in the 1960s and from the mid-1970s onwards this kind of theory developed rapidly.<sup>[42]</sup>

So-called  $MP_n$  methods – meaning Møller-Plesset theories of perturbation order  $n$  – were developed by, among others, the British-American theoretical chemist and later Nobel laureate John Pople.<sup>[43]</sup> Due to the works of Pople and his collaborators, the old Copenhagen paper of 1934 became much better known. Pople concluded that the original Møller-Plesset method carried



**Figure 4.** Number of citations per year 1935–2020 to the Møller-Plesset paper according to Web of Science.

to second and third order (MP2, MP3) had advantages over other methods and for small atoms and molecules agreed satisfactorily with experimental data. When Pople in 1998 gave his Nobel lecture in Stockholm, he praised the Møller-Plesset theory as an important step in the history of computational chemistry.<sup>[44]</sup>

The growth in visibility is illustrated by the number of citations (Google Scholar) to the Møller-Plesset paper in the six decades between 1962 and 2021:

1962–1971: 91. 1972–1981: 222. 1982–1991: 1070.  
1992–2001: 3570. 2002–2011: 5330. 2012–2021: 6100.

By far most of the many citations to the 1934 paper are in journals devoted to chemical physics and quantum chemistry.

The paper by Møller and Plesset is a prime example of what in the sociology of science is known as a “sleeping beauty.” This is a scientific paper whose relevance has not been recognized for a long time and then, more or less suddenly, becomes highly influential and cited.<sup>[45]</sup> Such sleeping beauties are of obvious interest from a historical and sociological point of view. Why were they initially ignored? Why did a sleeping beauty wake up at a particular, much later date?

A recent large-scale study of citation histories in all branches of natural and social sciences suggests that sleeping beauties are not exceptional and particularly not so in chemistry and physics.<sup>[46]</sup> The authors define a parameter called the “beauty coefficient” ( $B$ ) which expresses the number of citations a paper has received and how long after publication it gained them. It is so constructed that a paper which accrues citations linearly over time has  $B = 0$ , whereas one which languishes for 100 years before rising to fame can have  $B = 10,000$  or even more (for the full definition of  $B$ , see ref. 45). The

study in question lists the top fifteen sleeping beauties in science since 1900, seven of which it classifies as chemistry and five as physics. One of them is the Møller-Plesset paper of 1934, for which  $B = 2,584$  and the “awakening time” is found to be 1982. Another and much better known sleeping beauty, but with a beauty coefficient ( $B = 2,258$ ) a little less than that of the Møller-Plesset paper, is the famous Einstein-Podolsky-Rosen (EPR) paper of 1935 on the completeness of quantum mechanics.<sup>[47]</sup>

## 8. NOBEL PERSPECTIVES

It is well known that a large number of Nobel chemistry prizes have been awarded to scientists who were either physicists or whose work would be normally classified as physics.<sup>[48]</sup> On the other hand, no Nobel Prize in physics has ever been awarded to a chemist. Consider as an early example the 1908 chemistry prize to Ernest Rutherford for his contributions to radioactivity including “the chemistry of radioactive substances.” Bemused to have transformed so quickly from a physicist to a chemist, he wrote to Otto Hahn: “I must confess that it was very unexpected and I am very startled at my metamorphosis into a chemist.”<sup>[49]</sup> Many years later the 1951 chemistry Nobel Prize was awarded to Glenn Seaborg and Edwin McMillan for their discoveries of the first transuranic elements. While Seaborg was trained in chemistry under G. N. Lewis, McMillan was a nuclear physicist, such as he pointed out in his Nobel lecture. “In spite of what the Nobel Prize Committee may think, I am not a chemist,” he said.<sup>[50]</sup>

As mentioned, quantum chemistry was originally created by physicists rather than chemists and has to this day continued as an interdisciplinary field in which physicists play an important role. This is reflected in sev-

eral of the more recent Nobel Prizes. Thus, one-third of the 2013 prize was awarded to Michael Levitt, an Israeli trained in physics and molecular biology but not in chemistry. When Levitt was informed about the honor, he reportedly said, “I never studied chemistry, actually I’m a physicist. But that’s okay.”<sup>[51]</sup> The Nobel Prize awarded to John Pople and Walter Kohn in 1998 was the first and so far only one explicitly motivated in quantum chemistry. While Pople was a quantum chemist (or perhaps a chemical physicist), Kohn’s background was purely in theoretical physics. He wrote his doctoral dissertation under Julian Schwinger, one of the founders of modern quantum electrodynamics, and later changed to theoretical condensed matter physics. It was in this context that he developed the so-called density functional theory, a very successful approach to the many-particle problem which was widely considered an alternative to Møller-Plesset theory.<sup>[52]</sup>

Much like Møller and Plesset, Kohn was a theoretical physicist whose work unintendedly came to play a crucial role in quantum chemistry. Like Plesset had stayed at Bohr’s institute in the 1930s, where he met Møller, so 27-year-old Kohn came on a fellowship to Copenhagen to work in the same institute, where Møller was appointed his supervisor. In a report of 1953, Bohr and Møller wrote that, “In all his work Dr. Kohn has proved himself a highly qualified theoretical physicist with great knowledge of a wide field of problems.”<sup>[53]</sup> During Kohn’s stay at the Bohr institute, which lasted from July 1951 to September 1952, he participated in a large conference on problems of quantum physics attended not only by Møller and Plesset, but also by Heisenberg, Bethe, Pauli, and other quantum luminaries. However, he did not enter a collaboration with Møller, whose research interests at the time were quite different from his. When Kohn developed his density functional theory in the mid-1960s, Møller and Plesset had almost forgotten about their earlier work and none of them showed any interest in Kohn’s new approach or any other approaches to quantum chemistry.

## 9. CONCLUSION

The relations between physics and chemistry have changed significantly over time, often with physicists entering the field of chemistry with theories that most chemists found to be difficult and of no relevance to what chemistry is really about. The pioneers of quantum chemistry were theoretical physicists who had but little interest in traditional chemical problems and did not at all consider themselves to be chemists. The main

result of the present study is a slight reevaluation of the standard history of early quantum chemistry, or at least a supplement to it. While this standard history covers in considerable detail Hartree’s work and its extension to the Hartree-Fock theory, it has little to say about Fock’s contribution and even less about the one of Møller and Plesset. The two contributions, the one from 1930 and the other from 1934, had in common that they were one-time mathematical investigations not originally related to chemical problems.

The Møller-Plesset theory exemplifies to some extent how quantum theorists acted as “chemists without knowing it” insofar that much later the theory came to be seen as an important contribution to computational chemistry. Because the Møller-Plesset theory was a “sleeping beauty” with very little initial impact, it is perhaps understandable that it does not figure in historical writings on the early period of quantum chemistry. After all, it would be anachronistic to let our knowledge of the theory’s later development, say after the 1970s, influence the historical account of quantum chemistry in the 1930s. It is less understandable and harder to justify that the Møller-Plesset method has also been neglected in the writings on the more recent era, where extensions of this method have undeniably played a very significant role.

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