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Beyond computational difficulties: Survey of the two decades from the elaboration to the extensive application of the Hartree-Fock method

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ABSTRACT

The Hartree-Fock method, one of the first applications of the new quantum mechanics in the frame of the many-body problem, had been elaborated by Rayner Douglas Hartree in 1928 and Vladimir Fock in 1930. Promptly, the challenge of tedious computations was being discussed and it is well known that the application of the method benefited greatly from the development of computers from the mid-to-late 1950s. However, the years from 1930 to 1950 were by no means years of stagnation, as the method was the object of several considerations related to its mathematical formulation, possible extension, and conceptual understanding. Thus, with a focus on the respective attitudes of Hartree and Fock, in particular with respect to the concept of quantum exchange, the present work puts forward some mathematical and conceptual clarifications, which played an important role for a better understanding of the many-body problem in quantum mechanics.

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1. Introduction

The Hartree-Fock method is a well-known method of approximation for the treatment of the quantum many-body problem, applied nowadays to a plethora of different domains such as atomic, solid-state, and nuclear physics, quantum chemistry, and nanostructures. It was developed by two physicists, the Briton Douglas Rayner Hartree (1897–1958) and the Soviet Vladimir Fock (1898–1974). This process occurred in two stages, with works published in 1928 (Hartree, 1928a, 1928b, 1928c, 1929) and in 1930 (Fock, 1930). The method quickly proved to be the most adequate for many-body problems and later became the starting point of most techniques for describing atoms and molecules. Notably, from the mid-1950s onwards, it played a tremendous role in quantum chemistry. This was deeply connected to the development of digital computers,[1] which greatly facilitated calculations. Thus, since the Hartree-Fock method is known for leading to tedious computations, there is a tendency to view the years 1930 to 1950 as years of stagnation before its extensive use.

Nevertheless, the present paper emphasizes different aspects of the history of the Hartree-Fock method, and shows that the view that it all started with computers is only true to a certain extent. Already in the 1930s, the method, as presented by Fock, was the object of several considerations related to its mathematical formulation, possible extension, and conceptual understanding. To highlight them, we will mostly focus on Hartree and Fock. Not only because they played a central role as founders of the method, but also because they participated in its application in the 1930s and remained deeply connected with its further extensions.

The present study also helps us to extend some considerations developed in a recent article by James and Joas (2015) in which the authors emphasize the role of applications in establishing quantum mechanics and argue against the common tendency to put forth rather theoretical works. In particular, they insist on the period 1926–1928 where a number of applications participated in clarifying the unity, generality, and physical meaning of quantum mechanics. The Hartree-Fock method is, in our sense, another remarkable case study, which can be extended over a longer period.

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[1] For the emergence of digital computers from 1945 with the completion of the ENIAC, and their transformation during the 1950s and 1960s toward a more accessible commercial product, see Ceruzzi (1998).

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Its application pushed physicists not only to question the mathematical formulation of the quantum many-body problem, but also some of its physical consequences. Moreover, we intend to partially fill a gap in historiography, as specific studies of the Hartree-Fock method are missing so far.[2]

The present article proceeds as follows: Section 2 describes the elaboration of the Hartree-Fock method, with a special focus on Fock's contribution. Section 3 discusses mathematical and computational difficulties related to its early reception. Section 4 presents the different contributions of Hartree and Fock to the method during the 1930s. Section 5 then emphasizes conceptual issues concerning the quantum exchange phenomena and their reception by the two aforementioned actors. Finally, Section 6, in summarizing the situation of the Hartree-Fock method at the beginning of the 1950s, underlines the role played earlier by solid-state physicists in clarifying its conceptual understanding, but also places it in the larger dynamics of quantum chemistry at the dawn of the computer era.

2. The elaboration of the Hartree-Fock method

Let us begin with a brief account of the quantum many-body problem from a modern point of view. For a system of interacting particles, the Schrödinger equation proves to be too complicated to be solved and some sort of approximation is therefore needed. There exist different approaches, as for instance the Thomas-Fermi model, in which the system is considered in terms of electronic density,[3] or via recourse to individual wave functions as in the Hartree-Fock method. In the latter, the wave function of the system is factorized into a product of individual one-particle wave functions. This can take different mathematical forms, the *ansätze*, that represent different starting points for the resolution of the many-body problem. Physicists know about the importance of choosing the correct *ansatz*, which also must respect the various requirements of quantum mechanics. That choice must be considered as the *first issue* in our attempt to solve the quantum many-body problem. But there is also a *second issue*. By its very nature, the factorized form of the wave function does not represent the interactions between particles correctly. Therefore, the expression for the one-particle wave equations must be modified in order to "compensate" for this lack.

In the Hartree-Fock method, the actors dealt with these two "issues" differently. Hartree concentrated on the nature of the individual wave functions (*second issue*), while Fock focused on the question of the *ansatz* (*first issue*). The present paper mostly deals with questions raised by Fock's contribution. Hartree proposed a very powerful resolution of the *second issue*, and his work has already been discussed at length in the literature.[4] Thus, we will only make a few comments on Hartree's work, in order to provide some context, and will then put the emphasis on Fock's paper.

During World War I, Hartree worked in an Anti-Aircraft Experimental Section run by the British Ministry of Munitions. There, he developed an interest and significant abilities in numerical solutions to scientific problems. Later influenced by a set of lectures on quantum theory given at Cambridge by Niels Bohr in 1922, Hartree devoted his doctoral work at the Cavendish laboratory to the old quantum theory and applied his mathematical abilities to the application of numerical techniques in the study of atomic structures. In 1926, with the publication of Schrödinger's fundamental articles on wave mechanics (Schrödinger, 1926a, 1926b, 1926c, 1926d), he decided to apply the new quantum mechanics to his previous work.

The inaugural articles of the Hartree-Fock method were published in 1928 in the *Mathematical Proceedings of the Cambridge Philosophical Society* (Hartree, 1928a, 1928b, 1928c, 1929). The new approximate method for solving the many-body Schrödinger equation proposed by Hartree was based on individual wave functions. He then included the effects of the interactions between electrons by introducing a generalized potential, due partly to the field of the nucleus, and partly to the field generated by the core electrons. That potential was approximated using the following iterative method:

Initial field → Initial field corrected for each core electron[5] → Solutions of wave equation for core electrons → Distribution of charge → Final field

After iterative operations (i.e., by repeating this scheme), "self-consistency" is reached when the final field equals the initial field. That self-consistent field was considered by Hartree as characteristic of the atom studied, as it involves no arbitrary functions or constants. The method was naturally named the "self-consistent field method".

It should be made clear that Hartree had no need to examine the exact Schrödinger equation of the many-body problem. If we consider our *second issue*, the generalized potential introduced by Hartree was able to "compensate" the information lost using individual wave functions. But Hartree was not aware of this, and proceeded intuitively.[6] In the tradition of the old Bohr theory, he looked at electrons "as point charges revolving in orbits about the nucleus" (Hartree, 1928a, 89). Interested in their properties, within the frame of the new quantum mechanics he simply postulated the following Schrödinger wave equation for the motion of a point electron:

$$\nabla^2\psi + 2(E-V)\psi = 0,$$

where E is the total energy, and V the generalized potential due to the nucleus and the other electrons. It is only a few months later that the *ansatz* for the many-body wave function associated with such individual wave functions was made explicit by Slater (1928).[7] It is a simple product of *N* individual wave functions:

$$\Psi = \prod_{i=1}^{N} \psi(q_i)$$

Nevertheless, any theoretician aware of the developments in quantum mechanics at the time would have noticed that this *ansatz* was formally incorrect if used in the quantum many-body problem. Indeed, as early as 1926, Heisenberg and Dirac began laying the

[2] The method is discussed in Hartree's biography by his student Charlotte Froese Fischer (2003) and in John Clarke Slater's scientific biography (1975). However, Fock is generally under-represented in the secondary literature. A brief historical description of the elaboration of the Hartree-Fock method can also be found in Martinez (2017).

[3] Zangwill (2013) makes an historical parallel between Hartree's and Thomas's works. He shows how essential features of both approaches were combined and generalized in the mid-1960s by an approach to the electronic structure of many-electron systems called density functional theory (DFT), which is nowadays one of the most popular methods among both physicists and chemists.

[4] See for example Simões and Gavroglu (2000), Froese Fischer (2003), Park (2009), Zangwill (2013), or Martinez (2017). These references are especially helpful in reconstructing the genesis of Hartree's work in 1928. Froese Fischer (2003) is also a very valuable biographical source.

[5] Since an electron does not act on itself.

[6] See Slater (1963, 485).

[7] Slater (1928), and also Gaunt (1928), just before him, were trying to justify Hartree's method and his choice of working with individual wave functions. They proceeded by comparison with the results obtained within perturbation theory. On the early criticism of Hartree's work and the answers provided by Slater and Gaunt, see Park (2009, 54–55).

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