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# Origins of coupled cluster technique for atoms and molecules

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**Summary.** A short description of major events in the study of the correlation problem in the period 1950–1960 is given. The development of coupled cluster theory in the years of 1960–1972 is described. Selected references on the development of coupled cluster theory after 1972 are given.

**Key words:** History of coupled cluster theory – Correlation problem – Quantum theory of atoms and molecules

## 1. Introduction

I began my talk at the workshop with the remark that I spoke from a very personal point of view and therefore my statements were open to contest. Though not presented that way, I write this contribution in a very short form and I include only those facts which are generally recognized. Briefly, I list all papers which inspired my work and I mention what I consider as my contribution. In such a way I shall be safe from the historical point of view; the only possible error could be an error of unintentional omission.

In this article I describe two periods. The first period runs from 1950 to 1960 and the second period is given by the years 1960 to 1972. In the first period we shall trace several developments which were finally leading to the formulation of coupled cluster theory. Since 1960 we can already speak about the development of coupled cluster theory. This article is only about the origins of coupled cluster theory. I find the year 1972 a convenient closing point for the considerations presented in this paper. In the references there are selected major sources (review articles and books) which describe the further development of coupled cluster theory until today.

## 2. Problem of correlation effects and the development of coupled cluster theory

Around 1960 there were three outstanding problems in the quantum theory of atoms and molecules: the calculation of molecular integrals, seeking a satisfactory

solution of the Hartree–Fock problem for molecules and the problem of the correlation energy.

It should be noted that the correlation problem in nuclear physics and in the theory of electron gas was very much more difficult than in the theory of atoms and molecules. In nuclear physics there is a difficulty associated with the "hard core" character of nuclear forces and in the theory of electron gas, there is a difficulty related to the "long range" character of interelectron forces. Indeed, the standard Hartree–Fock does not make any sense in the theory of atomic nuclei or in the theory of nuclear matter. On the other hand, the second-order perturbation term in the energy of the electron gas (per particle) is infinite. Further, in the theory of nuclear matter and in the theory of the electron gas, the problems of extensivity are of crucial importance.

Therefore, it is not surprising that the first steps for the solution of the correlation problem were taken in nuclear physics and in the theory of the electron gas. We shall describe these developments until 1972. Further we shall describe the development in atomic and molecular physics since 1960 to 1972.

First we mention the theory of effective interaction in nuclear physics, which is today called Brueckner theory. Brueckner in a series of articles has shown how to modify the theory of the self-consistent field to be applicable to the problems of nuclear physics. The formalism of Brueckner was based on the concepts of nonrelativistic quantum mechanics. The best source for the understanding of Brueckner theory is the review article by Bethe [1], where Brueckner's ideas are formulated in a transparent way.

Brueckner intended to apply his theory both to finite nuclei as well as to the properties of nuclear matter. Brueckner was aware of extensivity problems and has shown [2] the validity of the linked cluster theorem up to the fourth order of the perturbation theory.

In another development Gell-Mann and Brueckner [3] have shown what is the nature of the difficulties related to the theory of the electron gas and proposed what we call today the summation of all ring diagrams.

In the year 1957 two articles were published which were of crucial importance to the further development of the theory of correlation effects. Goldstone [4] and Hubbard [5] have shown that the mathematical methods of quantum field theory are a very convenient tool for the study of correlation effects. In both articles the technique of diagrams was introduced. In the article by Hubbard it was noticed that the excitation operator had an exponential form.

Before turning to atomic and molecular physics let me mention that the first ideas of coupled cluster theory were formulated by Coester [6], Coester amd Kümmel [7], and by Kümmel [8]. They proposed the exponential ansatz as well as the idea of the construction of the equations for the cluster exponents by the use of commutators. The explicit equations were constructed about ten years later, in 1971–1972 by Kümmel [9], Kümmel and Lührman [10] and by Lührman and Kümmel [11].

Now we shall leave nuclear physics and give our attention to atomic and molecular physics. Let us mention two basic papers by Sinanoğlu [12]. In these papers Sinanoğlu introduced the idea of a cluster expansion based on an analogy with statistical physics. Further he formulated approximative equations for the two particle components. He neglected three particle collisions, putting them into a so-called "remainder". Sinanoğlu did not use second quantization and therefore his wave function had a rather complicated form.

Starting from 1962 Kelly [13] began to use Goldstone perturbation theory for a series of very successful atomic calculations.

In 1964 Primas [14] showed that the exponential ansatz is very important for the correct description of the dissociation of molecules.

I became interested in the theory of correlation effects in 1962 but only after reading the book by Tolmachev [15] was I able to reach a kind of synthesis of the above-mentioned ideas.

By this synthesis I mean a unified concept which would cover the work of Sinanoğlu, namely the so-called remainder, Brueckner theory of nuclear forces as well as Gell-Mann–Brueckner theory of the electron gas.

This was achieved in my Ph.D. thesis from 1965. In this thesis I derived a system of nonlinear equations for the components of the coupled cluster expansion using the methods of the time-independent formalism of quantum field theory. The use of the technique of diagrams was crucial for this undertaking.

Further, in the approximation $T = T_2$ I performed several coupled cluster calculations for the PPP model of benzene molecule. At this point I would like to underline that my equations for the components of the cluster expansion were in final, computer oriented form, formulated in terms of orbitals. All of these results were published in my paper [16] from 1966.

In the Spring of 1966, Joe Paldus and myself joined forces in coupled cluster theory and calculation. The first system which we studied was a sequence of cyclic polyenes. This work motivated our interest in the so-called Hartree–Fock instabilities (see, for example, a recent review [17]). In the Spring of 1967 we started the coupled cluster study of Be atom. Both of these projects were brought to conclusion only much later [18, 19].

The turning point in the study of correlation effects was the summer school organized by Lefebvre and Moser in Frascati, Italy, 1967. The state of the art from that time is well described in the proceedings of this conference [20].

To finish the description of the development of coupled cluster theory until 1972 I would like to mention two papers: In the first paper [21] we derived the coupled cluster equations in the approximation $T = T_2$ without the use of any technique of quantum field theory. The relevance of this work to some recent developments has been shown [22]. In the second paper [23] we calculated *ab initio* the ground state of $BH_3$. This was an important paper because it opened vistas for further use of the coupled cluster expansion in *ab initio* calculations. Further, in this paper the triexcited states were considered for the first time in the framework of coupled cluster theory.

The development and the use of coupled cluster theory after 1972 are described in several selected references [24–34].

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