The 1966 *Journal of Chemical Physics* Article by Jiří Čížek: What is in it and why is it so important

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Looking at the nine decades of the history of quantum chemistry and the present state of the treatment of the many-electron correlation problem, very few papers can be said to be more influential than the 1966 *Journal of Chemical Physics* article by Jiří Čížek [1]. This talk will discuss the content and significance of this relatively short, 11-page-long, paper, which has brought coupled-cluster (CC) theory to the forefront of quantum molecular science by introducing the exponential wave function ansatz of Hubbard [2] and Hugelnoltz [3] to electronic structure considerations and connecting it to the many-electron theory (MET) of Sinanoğlu [4]. We will demonstrate that unlike the earlier work by Coester and Kümmel [5], Čížek's 1966 paper shows how to use the exponential form of the wave function to solve the many-fermion Schrödinger equation in a computationally tractable manner. We will review how Čížek develops the necessary second-quantized tools, including creation and annihilation operators relative to the true and Fermi vacua, hole-particle formalism, normal products and contractions ("pairings"), and Wick's theorem, emphasizing the usefulness of normal-ordered form of many-body operators in CC considerations. We will then discuss his way of introducing the time-independent diagrammatic technique to handle many-body operators and their products and contractions and show how, equipped with all these tools, he derives the connected-cluster form of the Schrödinger equation, which, after projecting on the reference and excited Slater determinants, results in the system of polynomial equations for the energy and cluster amplitudes defining the single-reference CC theory, as we know it and use it until today. One of the most significant aspects of Čížek's 1966 work and the companion 1969 review [6], which have later inspired Bartlett and Purvis [7] and Pople *et al*. [8] to develop their initial general-purpose CC codes, is his presentation of the explicit algebraic equations in terms of one- and two-body matrix elements of the Hamiltonian and cluster amplitudes for the coupled-pair MET (CPMET), which is nowadays called the CC method with doubles (CCD). One might think that all of the above is more than enough for a 11-page-long paper, but, as shown in this talk, Čížek's 1966 paper has a lot more to offer. It compares the CC method with the configuration interaction (CI) approach and many-body perturbation theory and reports the first-ever CC calculations using the nitrogen molecule, treated *ab initio*, and benzene, treated via a semi-empirical Hamiltonian, as examples, comparing the results of CPMET = CCD computations with those obtained with CID, linearized CCD, and full CI. The latter work was enabled by Josef Paldus, who wrote the CCD program used in Čížek's 1966 work. Thus, other early papers on the CC theory co-authored by Čížek and Paldus [9] will be briefly reviewed in this talk as well. We will show how the 1966 paper by Čížek [1], followed by the 1967 [10] and 1969 [6] contributions and the early papers by Čížek and Paldus [9], have influenced later developments in CC theory, especially those in the 1970s and early 1980s.

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