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Perspective

Perspective on "On the correlation problem in atomic and molecular systems. Calculation of wavefunction components in Ursell-type expansion using quantum-field theoretical methods"

Čížek J (1966) J Chem Phys 45:4256

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Abstract. This is a personal perspective on the paper of Jiri Čížek that initiated the use of coupled-cluster (CC) theory in chemistry. As CC theory is now the method of choice for most highly accurate quantum chemical studies, its influence is profound.

Key words: Correlation problem – Coupled-cluster theory – Size-entensivity – Many-body theory – Diagrammatic methods

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Looking at the modern state of the treatment of the correlation problem in the electronic structure of molecules, few papers can be said to be more instrumental to that effort than the paper of Jiri Čížek in 1966, that first detailed the equations of the coupled-cluster (CC) approach. This too-brief, 11-page paper summarizes his dissertation work of 2 years earlier [1]. As the title says his use of "quantum-field theoretical methods" was intimidating to most quantum chemists of the time, which no doubt kept many from appreciating the significance of this work in 1966.

At that time, the best-known method for electron correlation in molecules was undoubtedly configuration interaction (CI). This tool had developed in the hands of Slater and Condon, with early applications by Boys, Parr, Matsen, and their coworkers around 1950 (see Ref. [2] for an excellent review). Somewhat less known to the quantum chemistry community was the parallel development in the mid 1950s of the correlation problem in physics that originated with Brueckner [3] and Goldstone [4], termed many-body perturbation theory (MBPT) because it was applicable to many-electron systems. This feature, that we now call size-extensivity [5], was not shared by CI, but was a necessity for the physics applications to nuclear matter and the electron gas. Important questions at this time included the correlation treatment of the high- and low-density electron gas, and in the first case it was possible to make an infinite sum of "ladder" diagrams to get a good answer, and in the other case, an infinite sum of "ring" diagrams; however, atoms and molecules have regions of both high and low electron density. Initial atomic applications of MBPT were made by Kelly [6]. Sinanoglu [7] and Nesbet [8] took some of the cluster ideas into the quantum chemistry community, though retaining many of the trappings of the more familiar CI world. Hence, the first complete solution of these diverse problems was offered by CC theory. In one convenient, conceptual, and computational framework it consolidates the infinite sum of ring and ladder diagrams and, indeed, all other kinds of diagrams, to offer a unified, size-extensive treatment of electron correlation.

The concept of an exponential wavefunction of a cluster operator

$$T = T_1 + T_2 + T_3 + T_4 + \cdots$$
$$\Psi = \exp(T)\Phi_0$$

for the correlation problem, where Φ_0 represents the wavefunction for an independent particle model such as Hartree–Fock and T_n the "connected" cluster operators for n electrons, is implicit in the linked-diagram expansion of Brueckner and Goldstone, and was, perhaps, stated most explicitly in a paper of Hubbard [9] in 1957. Hubbard gives the formula

$$\Psi = \exp\{S_L'(0)\}\Psi_0 \ .$$

The CC wavefunction had been considered by Coester and Kummel [10] as the "exponential S" ansatz at about the same time in the nuclear physics literature; however, none of these authors took the next step to develop explicit equations for the cluster amplitudes $\{t_{ijk\ldots}^{abc\ldots}\}$, which appear in the cluster operators,

$$T_n = \frac{1}{n!} \sum_{\substack{i,j,k,\ldots \\ a,b,c,\ldots}} t_{ijk\ldots}^{abc\ldots} \{a^\dagger i b^\dagger j c^\dagger k \ldots\}$$

and are the object of a CC calculation. To do this in a very general way required more powerful tools than the familiar rules based upon the Slater–Condon rules for matrix elements of the Hamiltonian between excited determinants; hence, the use of "diagrammatic methods". Čížek took his approach from a Russian language technical note of Tolmachev on "The field form of the perturbation theory applied to many-electron problems of atoms and molecules" written in 1963. In two pages, Čížek develops all the second-quantized tools he requires, defining the operators, their anticommutation relations, their normal ordered form, and their contractions or "pairings". He emphasizes the effective use of normal ordered operators and their contractions. This, in my opinion, still offers the most economical development of even algebraic second-quantized operator derivations, and is even more effective once we employ diagrams.

In the next six pages he introduces in rapid order H, T, S, R, and M skeleton diagrams, and all but the most avid reader is likely to be lost! In addition there is a need for "weight factors", equivalent line definitions, equivalent skeleton definitions which depend upon an appreciation of "topological deformations", open lines, closed lines, sign factors, etc. This leads to statements such as "In this special case, the M skeletons consist of a set of T skeletons (the empty set being included) each of which has two open paths. The possible R skeletons, having none or two open paths, which can be obtained from these M skeletons..." Whew! This is nothing less than a course on diagrams in six pages!

Using all the above, Čížek presents the explicit, spin orbital and spin-adapted CC doubles equations (CCD) i.e., $T = T_2$ (then called coupled-pair many-electron theory) in terms of one- and two-electron integrals over an orthogonal basis set. Assisted by Joe Paldus with some computations, he also reports some CCD results for N_2, which though limited to only π_u to π_g excitations, uses ab initio integrals in an Slater-type-orbital basis. He also does the full CI calculation to assess convergence, a tool widely used in Čížek's and Paldus' work and by most of us, today. He also reports results for the minimum-basis π-electron approximation to benzene.

Though used in some semiempirical applications by Paldus and Čížek [11] and one ab initio study [12] (see later), the CCD equations were not implemented into general purpose programs until 1978 by me and Purvis [5] and Pople et al. [13]. This general implementation included allowing for the open-shell case subject to an unrestricted Hartree–Fock reference function.

In another landmark paper, Paldus, Čížek and Shavitt [12] partly considered effects of other cluster operators, T_1 and T_3, in a minimum-basis ab initio study of BH_3. In 1982 we presented the detailed equations and implementation of CCSD for open and closed shells [14]. Two years later, we considered the initial effects of connected triple excitations (CCSDT-1) [15] and their noniterative inclusion CCSD[T] [16]. Today full CCSDT [17] and full CCSDTQ [18] are known and applied, and their noniterative forms such as CCSDT(Q_f) [19], and the ubiquitous CCSD(T) [20], which is a noniterative version of CCSDT-1 and a slight modification of CCSD[T] [21]; that adds the initial perturbative effects of triples to singles along with those due to doubles that define [T].[1]

For ground states (or the lowest state of a given symmetry) single-reference CC methods occupy the critical role in the now well-known paradigm of improving quantum chemical calculations: SCF < MBPT(2) ~ MBPT(3) < CCD < CCSD ~ MBPT(4) < CCSD(T) < CCSDT < CCSDT(Q) < CCSDTQ < full CI. Combined with systematically converging basis sets such as the cc-pVNZ basis [22], this sequence enables quantum chemistry to make reliable predictions about the structure, spectra, and most transition states for molecules with an ease of application that only requires a choice of basis set, level of correlation, and multiplicity, albeit with substantial computer time for CCSD(T) and beyond. These applications depend upon further extensions in the CC treatment of analytical gradients [23] and even Hessians [24]. The former provides first-order properties as a consequence of the "relaxed" and "response" one- and two-particle density matrices [21]. To quote Dunning, who comes from the multireference CI background, "...of the methods of widespread use today, the CCSD(T) method is the only one that provides a consistently accurate description of molecular interactions for all interaction scales investigated, from more than 200 kcal/mol to 0.02 kcal/mol" [25].

Now, depending only on a choice of basis and level of correlation just as for ground states, there are generalizations for the treatment of excited, ionized and electron-attached states [21, 26] and analytical gradients for such states [27]; for the treatment of second- and higher-order properties, static [28] and frequency-dependent [29]; for relativistic problems [30]; for explicit r_{12} CC theory [31]; and for various multireference generalizations of CC theory [32]. In brief, CC theory has now assumed a dominant place in the field of quantum chemistry, and it started with the pioneering efforts of Jiri Čížek and Joe Paldus.

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[1] Numerically, the doubles-to-triples effect [T] is approximately 95%–105% of the result, but the additional triples-to-singles part added in (T) is often numerically significant for difficult cases, and tends to reduce an overestimate of the correlation energy

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