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A BIOGRAPHY OF THE COUPLED CLUSTER METHOD

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The origins of the coupled cluster method are described. Special attention is paid to the arguments put forward for the exponential structure of the wave functions. Various approximation schemes invented during the last 40 years are presented. The problems arising from these approximations necessarily truncating or destroying the exponential form are discussed and ways to deal with them are described.

I am pleased to welcome my old friend Fritz Coester at this session. As you probably know he did play a seminal role in the invention of the Coupled cluster method (CCM). Besides, Fritz always was a benevolent observer and critic of the later developments of the method. I remember several discussions with him, where he quite often was quite critical about some aspects of the CCM,thereby helping me understand better my own work. I want to thank him for this — and for the many other occasions where he has helped me in various ways.

Having paid my respect to Fritz Coester let me now turn to the CCM. A biography not only describes the history of the person in question, it also is supposed to say something about its character. This can only mean that I have also to say something about the general features of the CCM and the ideas which lead to it. However, I shall say almost nothing about applications. I merely shall attempt to list the people who started applications in each of the many subfields of physics and chemistry.

1. Why the Exponential Form?

To understand the environment which led to the CCM I recall that in the mid fifties of the last century the many-body systems became the object of a lot of research papers. I remember a joke well known in the physics community before that time: *in physics there are either zero, one, two or (possibly) infinitely many particles.* This was because that was all one could do without computers or the kind of computers then available. This joke was not quite to the point since some Hartree–Fock (HF) variational computations had been done already, but by the quantum chemists (not by the physicists). It was perturbation theory in the Bethe–Goldstone or Green's function forms at which people jumped with great optimism at that time. Especially nuclear physics required a great amount of this optimism for two reasons: one had to find first some two-body nucleon-nucleon (NN) potential, either using fits from scattering experiments or deriving them from meson exchanges or a mixture of both, a somewhat dubious approach. Secondly, these potentials did necessarily have a hard or a strong repulsive core plus a somewhat long ranged attractive tail, and this fact somehow damped the hopes that perturbation theory could work. Due to Bethe[1] and Brueckner[2] in 1956 a way was found how to get around this problem by summing an infinite subset of perturbation diagrams describing the scattering of particle pairs in the nuclear medium. This was achieved by introducing a special two particle sub-wave function generated from such diagrams. There were doubts whether one could ignore the presence of other particles due to the rather long range of the attractive part of the NN interaction. This question was answered already in 1950 by Weisskopf.[3] He made the observation that the Pauli principle does not allow scattering into occupied levels of the Fermi sea and that this in coordinate space means the existence of the famous "healing distance" leading to rather short ranged effective potentials. This certainly was more or less only a plausibility argument to justify the special selection of perturbation diagrams. It finally lead to a systematic search for two-, three-, ... body sub-wave functions. In this search the need for dealing with hard core interactions psychologically was quite essential: The wave function has to vanish inside the hard core. Thus the free (unperturbed) part of the wave function must be compensated by something else and naturally the question did arise: what is this " something else"? The same phenomenon is to be expected for three particle scattering and so on. So there have to be a lot of cancellations to generate the regions where the wave function vanishes. And — going with it — a systematic procedure for approximations not destroying these internal cancellations has to be invented. There is no long way to come to the realisation that even for soft repulsive potentials the situation can't be very much different.

Let me — following the historical development — start with a situation where there is one single starting wave function (a "single reference state"), typically an exactly known ground state of a zero order (or "free") Hamiltonian. Examples, of course, are ground states of non interacting many-body fermion or boson systems (Fermi sphere, closed shell and Bose–Einstein condensate wave functions), or of field theories (bare vacua). Fortunately, there were some earlier papers, indicating or even explicitly showing that the exponential form of the wave function allows one — at least in most cases — to get all the insights needed. Since I have described these things in a former paper[4] I shall be rather short here. In quantum field theory Gell–Mann and Low[5] derived a ground state wave function Ψ_0 and energy E_0 within the realm of quantum field theory via perturbation theory.

$$|\Psi_0\rangle = \frac{U(0,\infty)|\Phi_0\rangle}{\langle\Phi_0|U(0,\infty)|\Phi_0\rangle} \quad \text{and} \quad E_0 = \frac{\langle\Phi_0|U(0,\infty)|\Phi_0\rangle}{\langle\Phi_0|U(0,\infty)|\Phi_0\rangle}\,, \tag{1}$$

with

$$U(0,\infty) = T\exp\left(\int_{-\infty}^{0} dt\boldsymbol{V}(t)\right) . \tag{2}$$

(where Φ_0 is the bare vacuum, T the time ordering operator and $\boldsymbol{V}(t)$ the interaction in the interaction representation). This, although being of a time ordered exponential form, can be considered as a precursor to the CCM, especially since the authors did prove that in the exponentials and in the energy only linked terms occur. The true breakthrough was due to Hubbard,[6] who by inspecting the time-independent perturbation series to all orders managed to prove that only linked clusters appear in the exponential form and that the energy consists of linked terms only. He also demonstrated that for extended homogeneous systems each such term and thus the energy itself is "*size-extensive*", i.e. proportional to the particle number. This was hard work and required a lot of detailed manipulations and rearranging of terms. Shortly after this Coester[7] reduced all this to a few almost trivial lines by using the exponential form as an Ansatz and then applying the Hausdorff expansion

$$\exp(-\boldsymbol{S})\boldsymbol{H}\exp(\boldsymbol{S}) = \boldsymbol{H} + [\boldsymbol{H},\boldsymbol{S}] + \frac{1}{2!}[[\boldsymbol{H},\boldsymbol{S}],\boldsymbol{S}] + \cdots \tag{3}$$

to prove the linked cluster theorem for the amplitudes in the exponentials. As a byproduct this proof was more general than Hubbard's since — without stating this explicitly- it was valid for finite systems as well as for fermions and bosons.

If I say that Fritz made the exponential *Ansatz*, I am in danger to provoke once again the widespread belief that this Ansatz has some artificial and arbitrary taint and that one could use as well another one. Indeed Rudolf Haag and Fritz Coester[8] very early had made quite clear that this form of the wave function is quite natural. They used the Bargmann space for their argument. Their reasoning is most easily presented for boson fields and thus I shall deal only with them. (For fermions one has to use Grassman variables.) Assume that everything may be represented by the Fock space in terms of the usual creation and annihilation operators $\boldsymbol{a}_i^\dagger$ and $\boldsymbol{a}_i$ and the bare vacuum Φ_0. In the Bargmann representation these operators are replaced by complex numbers as follows

$$\boldsymbol{a}_i^\dagger \to z_i \quad \text{and} \quad \boldsymbol{a}_i \to \frac{\partial}{\partial z_i} . \tag{4}$$

The analytic functions of $z_1, z_2, \ldots$ $f(z_1, z_2, \ldots)$ (abbreviated as $f(z)$) generate a Hilbert space with the scalar product

$$\langle f|g\rangle = \prod_i \left(\int \frac{dz_i d\bar{z}_i}{2\pi i}\exp(-z_i\bar{z}_i)\right)\bar{f}(z)g(z) , \tag{5}$$

and the states

$$|n_1, n_2, \ldots\rangle = \prod_i \frac{(\boldsymbol{a}_i^\dagger)^{n_i}}{\sqrt{n_i!}}|\Phi_0\rangle \to \prod_i \frac{z_i^{n_i}}{\sqrt{n_i!}} \tag{6}$$

define an orthonormal basis of Fock states. Making the (non-trivial!) assumption that the Hamiltonian has a discrete normalisable ground state Ψ_0, an arbitrary state can be written as

$$\Psi(z) = G(z)\Psi_0(z) \tag{7}$$

(because for bosons the ground state has no zeros). But then also the state created by

$$\boldsymbol{a}_i\Psi_0 \rightarrow \frac{\partial}{\partial z_i}\Psi_0(z) \equiv L_i(z)\Psi_0(z) \tag{8}$$

must have this feature. The solution of this equation is

$$\Psi_0(x) = \exp(S(z)) \quad \text{with} \quad L_i(z) = \frac{\partial}{\partial z_i}S(z)\,. \tag{9}$$

Here the general $S(z)$ is a superposition of polynomials

$$S(z) = \sum_n S_n(z) \tag{10}$$

with

$$S_n(z) = \sum_{i_1,i_2,\ldots,i_n} \frac{1}{n!}\int \cdots \int S_n(x_1,\ldots,x_n)z(x_1)\cdots z(x_n)\,, \tag{11}$$

where I switched to the coordinate representation. This clearly is the Bargmann analogue of the exponential wave function as used in the CCM. This derivation is valid also for one-particle systems, of course. But as such it does not really tell us anything about the quality of approximations, since necessarily any approximation will change the structure of the wave function. I shall come back to this aspect later in the context of the convergence of the CCM, where Arponen and Bishop[9] returned to the Bargmann space.

Let me now repeat a visualisation of the exponential structure, which also psychologically did play some role. This time I shall take extended Fermi many-body systems as an example.

One starts from the Slater determinant $|\Phi_0\rangle$ of occupied levels, describing in some sense the independent motion of all particles (Fig. 1). Then a pair of particles may interact throwing each other out of the Fermi sea. This is a contribution $\boldsymbol{S}_2|\Phi_0\rangle$ to the wave function with

$$\boldsymbol{S}_2 = \frac{1}{2!^2}\sum_{(i,j)\rangle k_F}\ \sum_{(l,m)<k_F} \langle i,j|S_2|l,m\rangle \boldsymbol{a}_i^\dagger \boldsymbol{a}_j^\dagger \boldsymbol{a}_l \boldsymbol{a}_m\,, \tag{12}$$

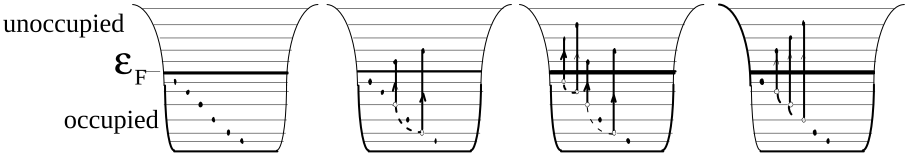

Fig. 1. Structure of Fermi ground state.

where k_F is the Fermi momentum (summation over pairs of holes and pairs of particles). Now it also will happen that two particles interact independently from each other. Their contribution is $\frac{1}{2}\boldsymbol{S}_2^2|\Phi_0\rangle$, with the factor 1/2 introduced to count each pair only once. Similarly for three pairs $\frac{1}{3!}\boldsymbol{S}_2^3|\Phi_0\rangle$ occurs etc. The total contribution due to all interacting pairs then will be $\exp(\boldsymbol{S}_2)|\Phi_0$. But it also may happen that a number of triples of particles interact independently of each other, thus leading in the same way to $\exp(\boldsymbol{S}_3)|\Phi_0\rangle$, and so on. For extended systems momentum conservation forbids occurrence of $\boldsymbol{S}_1$. For finite Fermi systems the Thouless theorem[10] tells us that the most general Slater determinant Φ_0' is related to a given one Φ_0 via $|\Phi_0'\rangle = \exp(\boldsymbol{S}_1)|\Phi_0\rangle$. Thus the complete exponential wave function

$$|\Psi_0\rangle = \exp(\boldsymbol{S})|\Phi_0\rangle \quad \text{with} \quad \boldsymbol{S} = \sum_{n=1}^{\infty} \boldsymbol{S}_n \tag{13}$$

(with $\boldsymbol{S}_n$ as proper generalisations of (12)) is recovered.

There is one more argument for the exponential, this time intermingled with the need to do approximations. Assume that the Hamiltonian has the usual form with finite-range interactions. Then, one may divide the space into spatially well separated cells labelled by k. To each cell belong operators $a^{(k)\dagger}(x)$ and $a^{(k)}(x)$ restricted to the cell k. The Hamiltonian becomes a sum

$$\boldsymbol{H} \approx \sum_k \boldsymbol{H}^{(k)} \tag{14}$$

and the wave function a product

$$\Psi_0 \approx \prod_k \Psi_0^{(k)} \tag{15}$$

with $\Psi_0^{(k)}$ different from zero only in cell k. Clearly only the exponential form with $\boldsymbol{S} = \sum_k \boldsymbol{S}^{(k)}$ — and $\boldsymbol{S}^{(k)}$ different from zero in cell k only — can combine both equations with the necessary "cluster property" of the functions S_n in coordinate space, implying that the latter vanish for large distances. This feature is closely related to what the quantum chemists have termed "size-consistency": the approximation by putting $\boldsymbol{S}_n = 0$ for all $n > N$ (termed SUBN or N-particle subsystem approximation by the CCM people) keeps this structure intact due to the exponential form of the wave function. Note also that this connection between cluster structure and exponential form has a long history in statistical mechanics, known as the Ursell–Mayer linked cluster expansion of the partition function.

This exponential structure at first sight looks so compelling and superior to any other one. In a naive theoretical sense it certainly is. But firstly from a practical point of view this is not always true. Here especially the correlated basis function (CBF) method[13] should be mentioned. Without doubt it is by far superior to the CCM for very high density systems like the helium fluid. I do not know whether anybody else has tried it with the CCM. I only remember that at Bochum around 1972 we completely failed in finding realistic ground state energies and thus did not dare to publish it. Probably a SUB4 approximation (something we could not do at that time) would be sufficient. Although this nowadays would be possible,it requires a much greater effort than using CBF. And nobody would be interested in doing this, especially in view of the excellent Monte Carlo[14] results. I regret very much that the combination of CBF and CCM we have developed in collaboration with E. Krotschek[11] never has been tried out.

Secondly, I want to make quite clear that any approach using a "zero order" or "unperturbed" Hamiltonian $\boldsymbol{H}_0$ is less compelling than one may think at first. Indeed, there is no a priori reason for the existence or use of such a $\boldsymbol{H}_0$. CBF, Monte Carlo and all what follows from the Jastrow variational program[12] are examples for very successful "theoretical physics (almost) without perturbation theory based on a $\boldsymbol{H}_0$". Thus we CCM believers should not overestimate our beloved technique. On the other hand, I still think that in the realm of methods based heavily on an $\boldsymbol{H}_0$ the CCM with its extensions is the most general and possibly the most powerful one.

2. Truncations and Symmetries

Of course, as said above, approximations have to be made. There are some different versions for the final approximate CCM equations, about which I later shall say more. In most of them the operator $\boldsymbol{S}$ is truncated via the SUBN approximation in the way described above. Having avoided spoiling the size-consistency one may ask whether there are other things spoilt by it. Indeed, already the first candidate, relativistic invariance, flunks the test. There are two ways to look at it. One of them is by realising that the diagrams on which the CCM is based are the non-covariant ones as obtained in the Goldstone time-independent perturbation expansion. The covariant Feynman diagrams are certain combinations of Goldstone's. A second argument is based on the observation that the boost operator applied to a truncated wave function will create out of a given $\boldsymbol{S}_n$ some new $\boldsymbol{S}'_{n'}$ with $n' > n$ and the truncation is spoilt. In summary, truncating the Feynman expansion keeps the relativistic invariance and it destroys the size-consistency, whereas typical (not all) approximations in the CCM do just the opposite. It is trivial that without approximations both are identical and that one therefore may hope that a sufficiently high order approximation violates relativistic covariance or size consistency only very little. One stringent test for the former in quantum field theory is the momentum dependence of the energy of a single meson, namely the form $\omega(k) = \sqrt{M^2 + k^2}$, where M is the *physical* mass. The worst case I could find in my notes is for the $1 + 1$-dimensional Φ^4 field theory[15] rather near the famous phase transition. The 6% deviation occurring in this example is a rare exception, it mostly is smaller than 1%. Such excellence proves the high quality of the underlying CCM SUB4 approximation.

Other symmetries, like the translational and rotational ones, are not necessarily and unavoidably violated by the CCM, although they pose serious technical problems. It is only fairly recently that the Manchester group has resolved this problem.[16] As far as I understand it, always the representation by harmonic oscillator states is essential. In our early nuclear physics work[17] we just subtracted out the centre of mass energy, but did not really use the relative coordinates in the Hamiltonian. Thus it was only an approximation, not always a very reliable one for very light nuclei like ^4He.

3. The Slow Start and the Complexity of the CCM

Considering the fact that the CCM was well understood around the late fifties it looks strange that nothing happened with it until 1966, as Jiři Čižek published his first paper on a quantum chemistry problem.[18] He had looked into the 1957 and 1960[19] papers published in Nuclear Physics by Fritz and myself. I always found it quite remarkable that a quantum chemist would open an issue of a nuclear physics journal. I myself at that time had almost given up the CCM as not tractable and, of course, I never looked into the quantum chemistry journals. The result was that I learnt about Jiřis work as late as in the early seventies, when he sent me a big parcel with reprints of the many papers he and Joe Paldus had written until then. I myself up to about this time did neither have the manpower nor the computer to do anything much beyond the work of Brueckner[2] (the SUB2 approximation for nuclei).

This now is the natural place to say something about the technicalities involved. Because of the often large number of terms in all versions of the CCM it is rather hard work to obtain the explicit equations by hand. And after this is done one has to write a program to put them into the computer. I feel that this offers an explanation why the quantum chemists jumped at the CCM before the physics community considered it in earnest: The chemists at that time were much more trained in the use of computers than the physicists, and after all without computers the CCM was quite useless. I believe that even today there are more applications on atoms and molecules than in all other fields together. But, of course, it became a great relief as people learnt do the routine (if you like, the engineering) part of the CCM by computer algebra. At present much of the applications are done in this way, both by the quantum chemists as well as by the physicists. The CCM equations are just made for computer algebra! This is a very desirable development, since after all as little manpower as possible should be invested for this "trivial" work.

4. Selecting a Truncation

Then, where is the non-"trivial" part, i.e. where is the physics besides in the selection of the Hamiltonian? There are only two occasions for the physicist to interfere: the truncation and the selection of the starting wave function Φ_0. Size consistency allows only what I have called SUBN approximation, i.e. putting all $S_n = 0$ for $n > N$. For hard-core potentials (or those with strong repulsion) actually a different truncation *must* be used in the CCM equations: using this naive SUBN approximation leads to infinite (or very large) terms. It can be most easily seen on the very lowest level, namely the unperturbed wave function: matrix elements $\langle ij|V|\,kl\rangle$ of the potential become infinite (or very large), where the labels $i, j, k.l$ refer to the SP states. The necessary systematic ("hard core") truncation scheme found nearly at the beginning of the CCM history[19,20] uses n-particle subsystem amplitudes. For two to four particles they are (q_i = occupied, p_i = non occupied levels, $\mathcal{A}$ = (anti)symmetrisation)

$$\begin{aligned}
\langle x_1, x_2|\chi_2|q_1q_2\rangle &= \mathcal{A}\langle x_1|q_1\rangle\langle x_2|q_2\rangle + \langle x_1, x_2|S_2|q_1q_2\rangle\,, \\
\langle p_1p_2p_3|\chi_3|q_1q_2q_3\rangle &= \langle p_1p_2p_3|S_3|q_1q_2q_3\rangle + \mathcal{A}\langle p_1|S_1|q_1\rangle\langle p_2p_3|S_2|q_2q_3\rangle \\
\langle p_1\cdots p_4|\chi_4|q_1q_2q_3q_4\rangle &= \langle p_1\cdots p_4|S_4|q_1q_2q_3q_4\rangle\,, \\
&\quad + \mathcal{A}\langle p_1p_2|S_2|q_1q_2\rangle\langle p_3p_4|S_2|q_3q_4\rangle \\
&\quad + \mathcal{A}\langle p_1|\boldsymbol{S}_1|q_1\rangle\langle p_2p_3p_4|\boldsymbol{S}_3|q_2q_3q_4\rangle\,.
\end{aligned} \tag{16}$$

They appear as such in the CCM equations often in the form of *finite* matrix elements $\langle i, j, \ldots|V\chi_n|k, l, \ldots\rangle$. This also answers the question put above: Inside the hard core $\langle x_1, x_2|S_2|i, j\rangle$ is just the amplitude making the wave function equal to zero. For three, four, ... particles things are a bit more complicated, but fully under control.[21] In general the CCM equations can be expressed completely in terms of these well defined "n-particle subsystem amplitudes" (sometimes termed "n-particle Bethe–Faddeev" amplitudes) χ_n. For $n = 3$ and 4, they have been used in nuclear physics.[17] Since this certainly is not the simple SUBN approximation of above the size-consistency is not preserved exactly. Would one, for instance, insist on the S_2 approximation to save size-consistency, i.e. use the wave function $\exp(\boldsymbol{S}_2)|\Phi_0\rangle$, then already the term $\frac{1}{2}\boldsymbol{S}_2^2|\Phi_0\rangle$ — as shown in the χ_4 amplitude of equation (17) — would be different from zero inside the hard core and generate infinities. This never has been a serious drawback since in nuclear physics size-consistency is a minor problem, in contrast to quantum chemistry where the relatively soft Coulomb interaction allows standard SUBN approximations and the size-consistency naturally is important in many cases.

5. Reference State

Another problem which always had to be considered, of course, was to find the best possible starting wave function Φ_0, the reference state. The early work considered only homogeneous extended systems with plane waves as the only possible single particle (SP) basis. The quantum chemists invariably use HF wave functions. For them there is no reason to do something else, because they have a large stock of these SP wave functions, developed (which is hard work!) and tested for many years. After all, this is a reasonable and very successful approach since the energy has been optimised via the Rayleigh–Schrödinger variational (RS) principle. But it is not always the best one. Indeed, in the case of Φ^4 field theory there is an enormous advantage in using the "maximum overlap" (MO) wave function as starting wave function: they are determined by maximising $|\langle\Psi_0|\Phi_0\rangle|$, where Ψ_0 is the exact ground state. In this case it so happens that the symmetry breaking version of this quantum field theory with MO could be treated everywhere, even near the phase transition of the symmetric counterpart, whereas the Hartree–Fock approach did fail there. Similar but less striking experience exist with other models. But there is another more technical aspect, namely that the CCM equation become quite a lot simpler: in the boson case with MO there is no S_1 and no S_2, or more generally, there is no one or two particle component in the wave function. For fermions S_1 vanishes; no one particle hole-pair components occur. It is true that one has to compute a new SP basis together with solving for the S_n (a fact, which makes MO impractical in quantum chemistry). But programming sometimes is greatly simplified because the number of terms is very much reduced due to the vanishing of all terms with S_1 and/or S_2.

In a sense more important than these more technical aspects for selecting a reference state are the symmetries of the latter: different phases require quite different reference states, and especially in quantum chemistry the various molecular configurations need to be implemented and tried out. One has to use some intuition, or, if available, information from elsewhere to find the right ones. Since 1991 there is a wealth of papers dealing with phase transitions in combination with CCM, mostly from the Manchester group.[23] In some cases the phases are known or there is an idea how they look like, and then it is fairly easy to make the right guess. Here MO sometimes may be helpful: For a true (local) maximum all eigenvalues of the second derivatives of the overlap $|\langle\Psi_0|\Phi_0\rangle|$ are negative at the stationary point. But if one or more of the eigenvalues should approach zero and even become positive as a function of some parameter, this indicates the onset of a new better reference state, describing a different shape or phase of the system.[24] Then one may use this new state Φ_0 from the outset. In quantum chemistry a more HF-like approach has been invented and applied by Bartlett:[25] instead of the overlap energy derivatives are used to search for optimal molecular configurations. In principle, any reference state not orthogonal to the exact state will do. But, the more of the features of the latter are incorporated in the former, the larger the overlap between exact and reference state and the better the approximation will be.

However, one has to realise that the overlap between the reference state Φ_0 and the *normalised* exact one $\exp(\boldsymbol{S})\Phi_0\rangle/\langle\exp(\boldsymbol{S})\Phi_0|\exp(\boldsymbol{S})\Phi_0\rangle$ in most cases is *extremely* small or formally equal to zero. Fortunately only some special parts of the wave function are relevant. For instance, for Fermi systems with two body interactions the energy can be written *exactly* as

$$E_0 = \langle\Phi_0|\boldsymbol{H}\exp(\boldsymbol{S})|\Phi_0\rangle = \langle\Phi_0|\boldsymbol{H}\left(1 + \boldsymbol{S}_1 + \frac{1}{2}\boldsymbol{S}_1^2 + \boldsymbol{S}_2\right)|\Phi_0\rangle\,. \qquad (17)$$

The higher $\boldsymbol{S}_n$ occur only in the equations for these amplitudes. If their influence is small — and this is the assumption on which all approximations are based — then on can hope for reliable values for the energy. Thus the small overlap is not necessarily a problem.

6. CCM Equations

So far I have enumerated features of the CCM for systems for which a single starting wave function Φ_0, i.e. an antisymmetrised or symmetrised product of SP states or a bare vacuum are sufficient. Very little has been said about the way the approximations actually are performed. Putting $\boldsymbol{S}_n = 0$ for $n > N$ leaves some freedom how to proceed further. There is the "normal" CCM (NCCM) which projects the Schrödinger equation onto a complete set of Fock states:

$$\langle \boldsymbol{a}^\dagger_{i_1} \cdots \boldsymbol{a}^\dagger_{i_n} \Phi_0 | \exp(-\boldsymbol{S}) \boldsymbol{H} \exp(\boldsymbol{S}) | \Phi_0 \rangle = E_0 \delta_{n,0} \,. \tag{18}$$

(From now on the creation operators $\boldsymbol{a}^\dagger_i$ are either creation operators for particles (bosons) or for particle-hole pairs (fermions).) This is the simplest way to get at results and therefore has been quite often the first choice. It has the advantage that for an interaction with a finite number of interacting particles or a finite power of field operators, the number of terms is finite. And even in cases with infinite powers — like the sine-Gordon field[22]— the terms can be summed in closed form. Nevertheless, this NCCM has aesthetic and practical disadvantages. Bra and ket are treated on quite different footing, because one projects on *free* Fock states only. Here Jouko Arponen, who has contributed so much to the understanding of the CCM, has found a sophisticated solution. He introduced two ideas[26] to partially or completely restore the symmetry between bra and ket: The problem arises first if one wants to compute expectation values of an operator $\boldsymbol{O}$ with the CCM wave function:

$$\langle O \rangle = \frac{\langle \Psi_0 | \boldsymbol{O} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \frac{\langle \exp(\boldsymbol{S}) \Phi_0 | \boldsymbol{O} | \exp(\boldsymbol{S}) \Phi_0 \rangle}{\langle \exp(\boldsymbol{S}) \Phi_0 | \exp(\boldsymbol{S}) \Phi_0 \rangle} \,. \tag{19}$$

Naively truncating via the SUBN approximation generates unlinked terms and therefore violates the Feynman–Hellman theorem which in turn is an indication of spoiling the size-consistency. This last feature is more or less evident from the inspection of the truncated series from which rather easily follows that there occur unlinked terms (and, by the way, the number of terms is infinite). This risk one may take if the S_n amplitudes are quite small and a low order expansion is good enough. It is better to follow Arponen: He did partially restore the bra-ket symmetry by parametrising the bra state as

$$\langle \tilde{\Psi}_0 | = \langle \Phi_0 | \tilde{\boldsymbol{\Sigma}} \exp(-\boldsymbol{S}) \,. \tag{20}$$

Here $\tilde{\boldsymbol{\Sigma}}$ is

$$\tilde{\boldsymbol{\Sigma}} = 1 + \sum_i \sigma_1(i) \boldsymbol{a}_i + \frac{1}{2} \sum_{ij} \sigma_2(ij) \boldsymbol{a}_i \boldsymbol{a}_j + \cdots \,. \tag{21}$$

$\tilde{\Psi}_0$ *would* be the exact bra *if*

$$\tilde{\boldsymbol{\Sigma}} = \frac{\exp(\boldsymbol{S}^\dagger)\exp(\boldsymbol{S})}{\langle\Psi_0|\Psi_0\rangle} \tag{22}$$

would be used in the expectation value defined as

$$\langle\boldsymbol{O}\rangle = \langle\tilde{\Psi}|\boldsymbol{O}|\exp(\boldsymbol{S})|\Phi_0\rangle\,. \tag{23}$$

Thus all excitations occurring in the bra are lumped together in the operator $\tilde{\boldsymbol{\sigma}}$. The remarkable and non-trivial feature of the energy expectation value $\langle\boldsymbol{H}\rangle$ defined in this way is that variation with respect to the amplitudes S_n and σ_n yields the CCM equations (19) and

$$\langle\Phi_0|\tilde{\boldsymbol{\Sigma}}\exp(-\boldsymbol{S})[\boldsymbol{H}, \boldsymbol{a}^\dagger_{i_1}\cdots\boldsymbol{a}^\dagger_{i_n}]\exp(\boldsymbol{S}|\Phi_0\rangle = 0\,, \tag{24}$$

which is a set of linear equations for the amplitudes σ_n. In addition $\langle\boldsymbol{H}\rangle$ in the form (24) trivially is the exact energy and identical with (19) for $n = 0$. (24) allows a rather simple evaluation of other expectation values. I admire the ingenuity of Arponen for inventing this seemingly strange form for the expectation value and showing that it is not at all strange, because in it are buried the exact CCM equations. I only mention that the resulting terms are linked, thus obeying the Feynman–Hellman theorem. Note, however, that there is no upper bound property connected with this variational principle. One may ask why one does not use the naive form (20) of the energy expectation value for the RS variational principle and varies with respect to the S_n amplitudes. The answer is that the resulting equations are too complex to be useful, for instance because they contain expectation values, which one does not know how to compute within this "old" formalism.

In the same paper Arponen[26] went one step further by using an exponential Ansatz $\tilde{\boldsymbol{\Sigma}} = \exp(\tilde{\boldsymbol{S}})$ also for $\tilde{\boldsymbol{\Sigma}}$. This has the advantage that the new $\tilde{S}_n$ amplitudes themselves are linked and a proper truncation conserves size-consistency. Naturally, this formalism, called "extended CCM" (ECCM) is both more powerful and more complicated than the NCCM. It is the most reliable method for describing different phases in terms of order parameters as expectation values of certain operators. Thus Arponen's work has led to a close cooperation with Ray Bishop and his Manchester group and finally to an enormous amount of important results in a wide range of objects from magnetism to lattice gauge fields.

Finally I should mention "local" versions of the CCM. In cases where S_n with high n are needed, but the high dimensionality of the S_n are a problem, one still can try to include them by restricting the range of the variables. For instance, in lattice spin models one may include only neighbours of a given site. This has been used at several occasions since 1990 by the Manchester group.[27] Also, in cases where one knows from other sources that some specific configurations are important, one may select S_n amplitudes which are adapted to them. As long as the reference state is not orthogonal to the exact one, anything is allowed. To include in addition to the standard (NCCM or ECCM) SUBN some specific S_n amplitudes with $n > N$ can only improve the results. In the worst case it may be useless.

7. Problems and Mathematical Background

Before going on to the more general CCM approaches, let me say something about the mathematical background of the method, the preliminary highlight being a paper by Arponen and Bishop.[9] Because the CCM can be characterised as some kind of improved perturbation theory, the problems of the latter sometimes will shine trough. There is the question of convergence. One warning signal came rather early. Applying the NCCM to the anharmonic oscillator[28–30] it was found that it is a very efficient method to obtain excellent approximations up to about S_6-approximations (SUB6). After that the results (compared to the exact one) deteriorate with oscillations typical for asymptotic convergence, finally to become useless. In addition, it became clear that the truncated wave function could not be normalised. However, in the paper by Arponen and Bishop mentioned before a mathematical analysis of the anharmonic oscillator has been performed showing that the Bargmann representation of the untruncated NCCM and ECCM equations and wave functions are well defined. Thus, both truncation and ordinary Hilbert space are the causes for the failures showing up in numerical solutions using CCM. At best asymptotic convergence can be hoped for. Since concrete results exist only for some one body systems, we cannot say anything definite about many-body ones. However, things can only become worse by going over to more particles. But this certainly is not specific to coupled cluster theories: we share this problem with more or less all branches of physics.

8. Generalisation to Multireference Systems and Excited States

I now go over to more complex systems: assume that a single starting wave function is not sufficient. This is the case for open shell systems, i.e. systems with some particles outside closed shells, or those with particles removed from the closed shell (excited states), or one particle states in field theories (technically identical with closed shells plus one particle) and so on. These systems are termed "multireference systems" in the literature.

I think the techniques for these systems were first obtained by the Bochum group in 1976,[31] although there seems to be a precursor by Mukherjee published in an Indian journal I could not lay hands on.[32] The explicitly linked form was invented two years later independently in Bochum[33] and in a more convenient form by Ingvar Lindgren in Göteborg.[34] These versions were different in appearance, but actually identical as long as no truncations were introduced. All versions have one thing in common: a basic ingredient is the ground state of the single-reference type, for example the closed shell system. (This idea actually is due to Fritz Coester who as early as 1969 mentioned it in a little known paper.[35]) The S_n amplitudes obtained via single-reference CCM are an input for the multireference equations. This makes sense only as long as the additional particles do not disturb the closed shell too much, i.e. the number of additional particles must be small compared to their total number and the excitation energies must be small compared to the total energy. In 1981 Emrich[36] invented a CCM for excited states of the same symmetry as the ground state, again using the ground state as input. All techniques can be summarised by the form

$$\boldsymbol{F} \exp(\boldsymbol{S})|\Phi_0\rangle \tag{25}$$

for the wave functions. Here $\boldsymbol{F}$ is an operator adapted to the problem at hand: for open shells it increases the number of particles to the desired number higher than the number of particles in the closed shell in all possible ways, creating holes in the shell and moving around particles in the levels above the closed shell, the "model space". For excited states of the same symmetry as the g.s. it generates all numbers of particle-hole pairs. For mesons in boson field theories it is a sum of creation operators. (In this case one has to start the iteration of the CCM equations with one, two, ... additional free particles if one is looking for one, two, ... meson states, since there is no particle number conservation.)

All methods have their problems. One is that there are practical (computational) limits to the size of the model space and, more seriously, the appearance of "intruder states", such that one may be forced to switch to an incomplete model space. This requires great care. To the best of my knowledge, Kaldor[37] was the first one to introduce this technique and Mukherjee[38] the first one to make it general and systematic and to resolve the size-consistency problems for such multi-reference systems. Also due to Mukherjee is the idea of applying the operator $\exp(\boldsymbol{S})$ on a *set* of reference states.[39]

9. Temperature- and Time-Dependence

Time-dependent forms of the NCCM were introduced independently by Monkhorst[40] in 1977 and Negele[41] in 1978. For the ECCM Arponen, Bishop and Pajanne found a very general description in 1987.[42] Mukherjee introduced a multireference time-dependent CCM in 1987.[43] I do not go into any details here, since to my knowledge there are relatively few applications. Finally I have to mention another contribution to the CCM by D. Mukherjee: he was the first one to develop a trustworthy temperature-dependent CCM.[44] I must admit that I do not know the present status of applications of this method to realistic problems.

10. Applications

During the past 40 or so years the CCM has invaded one branch of Chemistry and Physics after the other. It is quite impossible to give a complete overview of everything which happened until today. Instead let me present a (possibly not complete) list containing the dates and the authors of the first applications in each individual field.

First applications in various fields

1966	Quantum Chemistry, J. Čižek[18]
1973	Finite Nuclei, H. Kümmel and J. G. Zabolitzky[45]
1977	Finite dimensional models, K. H. Lührmann[46]
1978	Electron gas, R. F. Bishop and K. H. Lührmann[47]
1981	Nuclear matter, B. D. Day and J. G. Zabolitzky[48]
1982	Finite dimensional models with ECCM, J. Arponen[49]
1985	Quantum field theory, C. S. Hsue and H. Kümmel[50]
1988/9	Electroweak Interaction (relativistic) effects, I. Lindgren, J. Lindgren and A. M. Mårtensson;[51] S. A. Blundell, W. R Johnson and J. Sapirstein;[52]
1990	Spin lattice models (ECCM), M. Roger and J. H. Hetherington[53]
1990	Energy derivatives, (molecules), E. A. Salten, G. W. Truck and R. J. Bartlett[25]
1993	Lattice gauge fields, R. F. Bishop, A. S. Kendall, L. Y. Wong and Y. Xian[54]
2001	From hearsay: Solid states, Biophysics

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