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# Coupled-cluster theory in atomic physics and quantum chemistry

## Introduction and overview

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The articles in the present and four subsequent issues of Theoretica Chimca Acta derive from a Workshop on Coupled-Cluster Theory at the Interface of Atomic Physics and Quantum Chemistry, organized by the author and Dr. B.P. Das, Utah State University, on August 6–11, 1990, at the Institute for Theoretical Atomic and Molecular Physics of the Harvard-Smithsonian Center for Astrophysics. The workshop brought together two different groups of scientists who had previously had little interaction, but who were linked by the need for high accuracy in correlated calculations of electronic structure in atoms and molecules. One group consisted of experts in coupled-cluster (CC) and many-body perturbation (MBPT) approaches for electron correlation in molecules, who had developed these tools for determining molecular structure and spectra using CC/MBPT methods. The second group was primarily concerned with employing many-body techniques in important applications to weak interactions in atoms. The following introductory remarks provide an overview of the subjects discussed at this meeting.

## Parity violation in atoms

The subject of weak interactions in atoms falls into two categories: (i) Parity violation in atoms due to neutral weak interactions; (ii) Electric dipole moments of atoms due to parity and time-reversal violation. The standard electroweak unification model of Weinberg and Salem predicts a parity violating neutral weak interaction between the constituents of an atom in addition to the usual electromagnetic interaction.

The neutral weak interaction, which is mediated by the $Z_0$ particle, mixes states of opposite parities; thereby giving rise to an electric dipole transition between states of the same symmetry. Several ingenious experiments have been carried out on atomic cesium, thallium, bismuth and lead to detect such an electric dipole transition. The most accurate experiment to date is on cesium where the electric dipole transition moment has been measured to an accuracy of 2% by Wieman and co-workers. The accuracy of the measurements on bismuth and thallium are soon expected to match that of cesium. The experimental results when combined with accurate relativistic many-body calculations confirm the validity of the standard model. If the combined accuracy of the atomic experiments and calculations improve, it may be possible to draw certain conclusions about a variety of unification models that go beyond the standard model.

In addition, it is a well-established fact that an atom can possess a permanent electric dipole moment (EDM) if parity and time-reversal violating interactions between the constituents of an atom exist. Since parity violation has been observed earlier, the significance of observing a permanent EDM is that it would be the first ever direct signature of *T* violation. Furthermore, the combined results of atomic EDM experiments and calculations can shed light on the origin of CP violation; one of the most challenging problems of contemporary physics.

## Coupled-cluster theory

The high accuracy required for the calculation of parity violations in atoms as well as for the calculation of molecular energy differences of chemical significance calls for extreme accuracy in the solution of the electron correlation problem. The coupled cluster (CC) method as developed by Coester, Kümmel, and Čížek is excellently suited to such levels of accuracy. The origins of the method are discussed in the contributions of Kümmel and Čížek[1]. The further developments of these approaches for chemistry was summarized at the workshop by Bartlett. The content of this talk has been published previously [(1989) J Chem Phys 93:1697]. For physics, the progress was described by Bishop and this report is included here. The range of applications and the degree of accuracy achieved in the past decade attests to the effectiveness of the coupled cluster methods. However, to treat all problems with the full power of this theory requires additional elements in it to be formulated, improved, or implemented. They include:

- Dirac-Fock based relativistic CC theory
- Open-shell single and multi-reference CC approaches
- CC methods for excited states
- CC methods for the treatment of properties

Each of these requirements further generates several competing approaches discussed at the workshop that can be recommended by various criteria.

In the following some attempt, admittedly a personal one, is made to summarize some of the profitable areas of attack identified at the workshop that should lead to important developments in the field.

## Current problems of coupled-cluster theory

### *Multi-reference coupled-cluster* (MRCC) *generalizations for excited states and potential energy surfaces*

For excited states, ionization potentials, electron affinities, and Auger spectroscopy, Fock space multi-reference methods are nearing a wide and routine level of

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[1] In the following references will be limited to names of the authors who discussed the topic at the workshop and whose papers in the proceedings should be consulted for a more detailed analysis and prior references. When a topic is mentioned that is not represented adequately in the Proceedings, a more complete reference to the work is provided

applicability (as discussed at the workshop by Mukherjee, Kaldor, and Rittby). Important contributions remain, however, in determining transition moments, using open-shell reference states, and in separating the true correlation effects from the somewhat artificial "spectator" terms that emerge in the Fock space theory. For example, the latter prohibits a Fock space MRCC method limited to all single and double excitations (MRCCSD) from giving the correct answer for the two-particle problem [Meissner, Bartlett (1991) J Chem Phys 94:6670], since some Fock space $S_3$ operators of spectator type appear even for two particles.

However, the greatest weakness in the current Fock space approaches is the necessity of a single determinant closed-shell description for the reference state. Often such a suitable reference state is far from the state of interest. Using new, QRHF and ROHF based single reference CC solutions (see Open-shell CC methods below) as the reference state offers a critical improvement that should make Fock space MRCC far more applicable. The alternative Fock space approach of Barysz, Stolarczyk, and Monkhorst is also addressed in the proceedings.

The different Hilbert space MRCC (Paldus, Jeziorski, Meissner, Balkova) would not have the above problems and unlike Fock space MRCC, which derives from a single reference ground state description, it also provides for multi-configurational ground states. The Hilbert space approach replaces the "hierarchical waveoperator" of the Fock space approaches with another operator. In principle, this waveoperator should be simpler to use, as it does not have to simultaneously describe the correct eigenstates of all $N-1$ and $N+1$ electron states in addition to the $N$ electron states. Some of the first results reported using the Hilbert space method were presented at the meeting (Balkova et al., Paldus et al.).

An important development presented at the meeting was the generalization of the Hilbert space MRCC to *incomplete* active spaces [Meissner, Bartlett (1990) J Chem Phys 92:561]. This makes the theory primed for a burst of computational activity. Although this helps to alleviate the severe problem of intruder states, the intruder state problem is still endemic to the method. Much activity in this area will be reported in the next few years.

In particular, the Hilbert space, two-configuration (prediagonalized) method provides the theory for the facile implementation of an open-shell singlet CC method, the *bête noire* of all "single reference" many-body programs; such calculations should be made with equal efficiency to current single determinant reference CC examples.

### *Equation-of-motion* CC *methods*

Besides MRCC methods, excited and ionized states can also be treated by equation-of-motion (EOM) CC methods [Bartlett, Mukherjee, Meissner; see also, Geertsen et al. (1989) Chem Phys Lett 164:57; Nakasuji, Hirao (1978) J Chem Phys 68:2053]. EOM-CC is also called CC linear response theory [Monkhorst (1977) Int J Quantum Chem S11:421]. These methods are potentially of very general applicability. For ionization potentials, EOM-CC will give the principal IP's and "shake-up" effects while the current Fock space method has to be extended to obtain the shake-ups. EOM-CCSD will also describe excited states dominated by either single or double excitations, although the current

Fock space MRCC can only describe states derived from single excitations. EOM-CC does not provide entirely (size)extensive results for excited states (Meissner, Bartlett, op. cit.). According to Mukherjee's remarks at the workshop, they can be said to be "valence extensive", however, meaning that the extensivity errors should not be nearly as great as in CI type methods. Such methods also offer a route toward time-dependent properties (Liu, Kelly, Sekino). Research in the area of time dependent CC theory is likely to pay important dividends in the future.

### *Properties and analytic derivatives*

In molecular theory, it is essential to analytically evaluate the derivative of the energy with atomic displacement to effectively search potential energy surfaces. The theory for first derivatives of single reference CC methods has been developed since 1984 [see e.g. Bartlett (1986) in Geometric derivatives of energy surfaces and molecular properties, Reidel, Dordrecht, p. 179; Salter et al. (1989) J Chem Phys 90:1752]. Implementations of the relaxed density approach for gradients on potential energy surfaces for closed shell molecules at the CCSD level have been available since 1987 [see Scheiner et al. (1987) J Chem Phys 87:5361]. Recently, these methods have been generalized to open-shell UHF, ROHF or (quasi)QRHF references [Gauss et al. (1991) J Chem Phys 95:2623, 2639; (1991) Chem Phys Lett 182:207].

The principal idea in all analytical derivative (property) methods is the introduction of the so-called "relaxed" density that in CC/MBPT takes the place of an ordinary expectation value density as an essential computational and conceptual tool. That is,

$$E^{\alpha} = \langle H^{\alpha} \rangle = \langle o \,|\, \Lambda H^{\alpha} \exp(T) \,|\, o \rangle \,.$$

The relaxed density element, $D_{pq} = \langle o | \Lambda a_p^{\dagger} a_q \exp(T) | o \rangle$. $H^{\alpha}$ is the derivative of the second-quantized Hamiltonian. The rôle of $\Lambda$ is to replace the first-order perturbed wavefunction with a perturbation independent quantity that satisfies a linear equation. In this way, $D_{pq}$ is independent of any perturbation. Furthermore, all orbital relaxation effects are contained in the **D** density. This procedure also provides a route toward other properties, as first derivatives with respect to other parameters than nuclear displacements. Hence, all "first-order" properties like dipole and quadrupole moments, field gradients, etc. are routinely available from $\Sigma\, D_{pq} \Theta_{pq}$ when $\Theta$ represents the operator.

The alternative of simply taking the expectation value of a CC wavefunction, $E^{\alpha} = \langle o | [\exp(T^{\dagger}) H^{\alpha} \exp(T) \rangle_C | o]$ has two problems. The first is the expectation value of the exponential wavefunction does not terminate and forces truncation. The second is the CC wavefunction does not exactly solve the Hellmann-Feynman theorem which makes the derivative and expectation value differ. In practice, however, for many ordinary one-particle properties (gradients not included) the expectation value of a CC method with triples truncated to fourth order tends to work well [see Noga, Urban (1988) Theor Chim Acta 73:291].

Second-order properties in addition to force constants, like polarizabilities, spin-spin coupling constants, dipole derivatives, and others, are not yet obtainable purely analytically, but would instead require numerical differentiation of analytically computed first derivatives. Clearly, the analytical evaluation of such higher-order properties would be highly desirable. The generalization to higher order analytical derivatives is not easy, although the theory has been presented [Salter, Bartlett (1989) J Chem Phys 90:1767] and a preliminary implementation made [Koch et al. (1989) J Chem Phys 92:4924].

### *Alternative ansätze in* CC *theory*

Closely tied to the question of properties in CC theory is that of alternative ansätze for CC-like wavefunctions. That is, instead of standard CC theory, modifications can be made without jeopardizing the fundamental rationale for CC theory, namely the extensive property, while offering some alternative advantages that normal CC theory does not have. An example is the imposition of a stationary principle for an energy functional derived from an alternative wavefunction ansatz. The expectation value (XCC) and unitary (UCC) methods fall into this category (Kutzelnigg, Bartlett). Unlike normal CC, where closed form equations are obtained for $T$ amplitudes, the XCC approach starts from

$$\langle o|(\exp(T^{\dagger})H\exp(T))_{C}|o\rangle$$

and the unitary (UCC) approach begins with

$$E=\langle o|\exp(\tau^{\dagger})\,H\exp(\tau)\,|o\rangle$$

for $\tau=T-T^{\dagger}$, which does not terminate. This necessitates truncation and variation, $\delta E/\delta T^{\dagger}$, to define equations for the amplitudes in $T$ (and $\tau$). However, unlike normal CC theory, such variation results in the UCC wavefunction satisfying the generalized Hellmann-Feynman theorem, i.e.

$$\frac{\partial E}{\partial \alpha}=\langle o|\exp(\tau^{\dagger})\,H^{\alpha}\exp(\tau)\,|o\rangle_{\mathrm{TRUNCATED}},$$

where the expression for the derivative has to be truncated in the same way as the energy functional itself [Bartlett et al. (1989) Chem Phys Lett 155:133]. This makes it far easier to obtain analytical derivatives. UCC and XCC results have been reported [Watts et al. (1989) Chem Phys Lett 157:359] and presented at the workshop.

Another advantage to the unitary approach is that Hermitian symmetry is maintained throughout all the equations. This, too, differs substantially from the inherently unsymmetric normal CC method and has the advantage that important higher-order correlation corrections can be introduced much more tractably than they would be in normal CC. This fact has formed the basis for iterative and non-iterative $T_4$ corrections to CCSD and CCSDT methods (Bartlett). In his contribution to the Proceedings, Kutzelnigg uses an error analysis to argue that more general projected expressions than that usually used offer a more accurate procedure.

### *Extended* CC *theory*

Extended CC theory (Arponen, Bishop) is another approach that offers an alternative ansatz in CC theory, with particular relevance to properties. A property like $E^\alpha = \partial E / \partial \alpha$, may be written in ECCM as

$$E^\alpha = \langle o | \exp(\tilde{\Sigma}) H^\alpha (\exp \Sigma) | o)_{\mathrm{DC}},$$

where the DC indicates a double connected structure. Unlike the unitary approach and closer to the first approach for properties in the normal CC theory, where $\Lambda$ would be the first approximation to exp $(\tilde{\Sigma})$, $\tilde{\Sigma}$ and $\Sigma$ depend upon different amplitudes, requiring that twice as many be obtained as in the UCC or XCC methods. However, unlike normal CC, ECCM offers a structure that requires that all amplitude diagrams be connected from above and below ($\Lambda$ is not entirely connected, e.g.). CI coefficients are not connected at all, while normal CC only has the amplitude expressions connected from the bottom. It is argued the fully connected structure is essential in correctly describing more difficult situations including phase transitions (Arponen, Bishop). Also, unlike UCC, the ECCM equations naturally terminate as do the normal CC equations, but with higher order and more complicated contributions.

### *Recursive intermediate factorization*

From the computational viewpoint, an important result discussed in the proceedings (Kucharski, Bartlett) is that the highly non-linear CCSDTQ equations can be entirely represented "linearly" in terms of generalized matrix products of recursively computed intermediates, none of which depend upon more than a single $T$ amplitude. This forms an essential framework for anticipated application of high order CC methods, with CCSDTQ recently being presented (Kucharski and Bartlett, Chem Phys Lett, in press).

### *Relativistic* CC *methods*

The need for a coupled-cluster method that is suitable to relativistic phenomena is apparent. For atoms, relativistic linearized CC methods have been used for parity violation in Cs, as discussed at this workshop (Blundell, Sapirstein, Hartley, and Martensson-Pendrill). Yet the power of CC theory lies in the non-linear terms, so these must be included as well. Also, no attempt to do molecules with a correct relativistic approach has yet been made. For atoms, real orbitals may be used, but for molecules the necessity of employing complex orbitals throughout the calculation complicates the programming, but this is an important area for advancement (Sekino, Das, Mohanty).

Mohr and Sapirstein further emphasized the importance of quantum electrodynamic effects in high-$Z$ ions, particularly electron-electron interactions on the self-energy and two photon exchange corrections.

### *Moment approach in* CC *theory*

The indirect inclusion of additional correlation effects in CC theory also drew attention (Jankowski, Paldus). It was demonstrated that requiring least-squares satisfaction of the single excitation projection of $\exp(T_2)$ along with the double excitation projection, which is an overdetermined set of equations, enables avoiding a singularity that occurs in the linearized (LCCD) equations. Similar techniques could potentially be exploited to include certain effects of triple excitations (an $n^7$ procedure) indirectly in a computational scheme effectively limited to just single and double excitations (an $n^6$ procedure).

## *Open-shell* CC *methods*

The description of open-shell systems with CC theory can be accomplished in single and multi-reference forms. The former benefits from the same ease of application as the single reference closed-shell theory and may be accomplished with an unrestricted Hartree-Fock (UHF) reference, or a restricted open-shell HF (ROHF) reference [Rittby, Bartlett (1988) J Phys Chem 92:3033]. A third open-shell method uses a quasi-restricted HF (QRHF) reference (Rittby, Bartlett, op. cit.) which constructs a high spin open-shell reference from a set of orbitals taken from an adjacent, usually closed-shell state by adding or deleting an electron. Since the latter function is not variationally optimum for the particular problem at hand, it is only a viable starting point because of the $\exp(T_1)$ operator in a coupled-cluster wavefunction, $\exp(T_1+T_2+\ldots)|o\rangle$, as $\exp(T_1)$ builds in the flexibility to rotate the orbitals as necessary for the problem. In the UHF case, $\exp(T)|\mathrm{UHF}\rangle$ is not an eigenfunction of spin, while an ROHF based method satisfies the projected spin eigenfunction property, $\langle \mathrm{ROHF}|\hat{S}^2\exp(T)|\mathrm{ROHF}\rangle = S(S+1)$ as does the QRHF equivalent. This is often important for highly spin contaminated cases. Several examples were presented by Scuseria.

A further rotation of the CC equations to make $T_1=0$ defines Brueckner orbitals, so the reference determinant becomes the determinant that has maximum overlap with the exact wavefunction. Such CC(B) methods are sometimes useful (Lauderdale et al., Chem Phys Lett, in press).

An MBPT analogue of the above ROHF-CC method is possible and offers a highly efficient, non-iterative, correlation method that is much preferred to UHF-MBPT when spin contamination is a problem. Hubac and Čársky discuss a different ROHF-MBPT procedure in the proceedings.

Whereas, the wavefunction $\exp(T)|\mathrm{ROHF}\rangle$ is not an eigenfunction of spin, it is possible to rigorously formulate a ROHF based CC method that is. This was discussed by Janssen at the workshop [Janssen, Schaefer (1991) Theor Chim Acta 79:1]. Another approach that applies to the same problem was discussed by Jeziorski et al. The related use of a more general valence bond type reference in CC theory was discussed by Čížek.

## *Intruder states*

The resolution of intruder state problems in CC theory is critical to viable multireference techniques. A particularly incisive analysis was offered by Morgan, who demonstrated its resolution in high-order perturbation theory studies.

## *High accuracy basis sets*

The need for extremely high numerical accuracy in many problems including parity violation recommend the use of new, numerical or explicitly correlated approaches in many-body methods. Drake employed Hylleraas type explicitly correlated functions in his highly accurate results for Rydberg states of He, while Szalewicz, Zabolitzky, Jeziorski, and Monkhorst report excellent CC results using explicitly correlated functions for small molecules [see (1984) J Chem Phys 81:2723]. Morrison considered spline type functions to obtain effectively numerical accuracy in many body calculations. Scuseria reported on the use of atomic natural orbitals (ANO) in high level CC applications. Kutzelnigg reported on successes with adding explicitly the effects of the $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ cusp.

### *Vibronic corrections*

The coupling between electronic and vibrational motion including alternative approximations to the standard Born-Oppenheimer procedure was also addressed (Hubac) [see Hubac et al. (1989) Lecture Notes in Chemistry 52:95].

## Summary

Summarizing the meeting briefly, many quantitative examples were shown which demonstrate the high accuracy of CC methods for electron correlation, compared to other *ab initio* approaches. Generally, more accurate energies, frequencies and properties of molecules were obtained with less computational effort. Possible exceptions are the problems requiring extensive non-dynamic correlations whose multi-reference character can make large MR-CI calculations superior. Extremely accurate results have also been obtained, even with linearized CC methods, for the $(6s-7s)$ transition moments of cesium, essential to the parity violation problem (Blundell, Sapirstein, Mårtensson-Pendrill). Attacking yet more difficult problems, CC methods were shown to reliably describe spin lattices (Bishop) and various kinds of model systems (Paldus, Čížek), including the description of phase transitions (Bishop, Arponen). Current CC methods are thus among the most powerful available for many diverse problems, even transcending electronic structure. Moreover, they are being continually improved, e.g. through multi-reference generalizations, a fact that bodes well for the future.

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