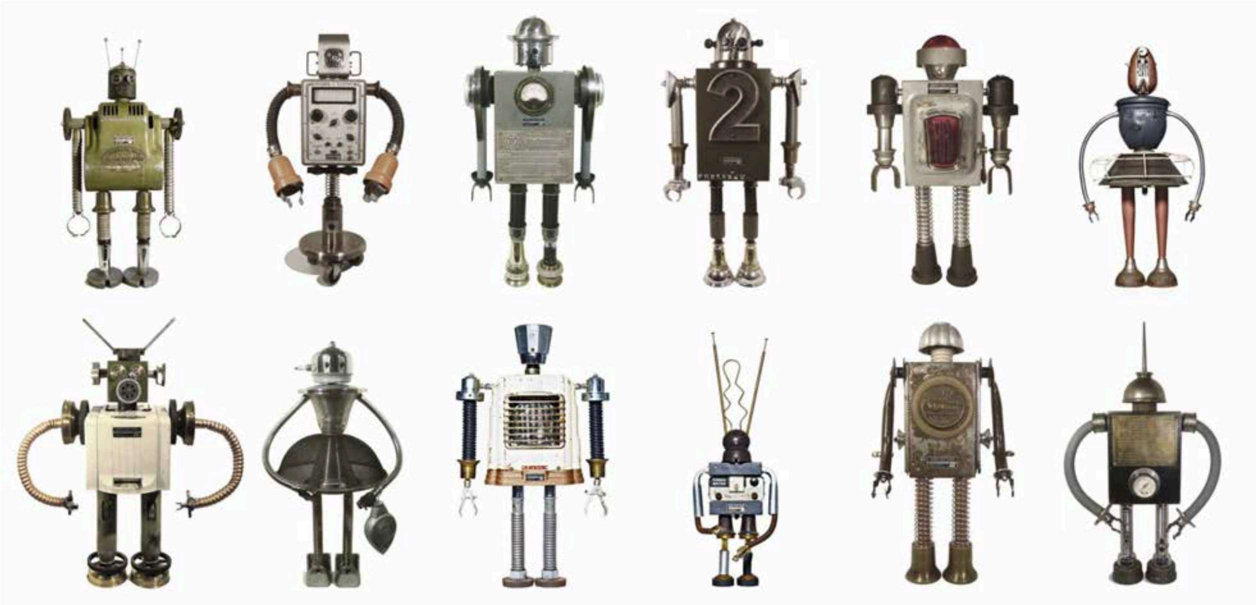
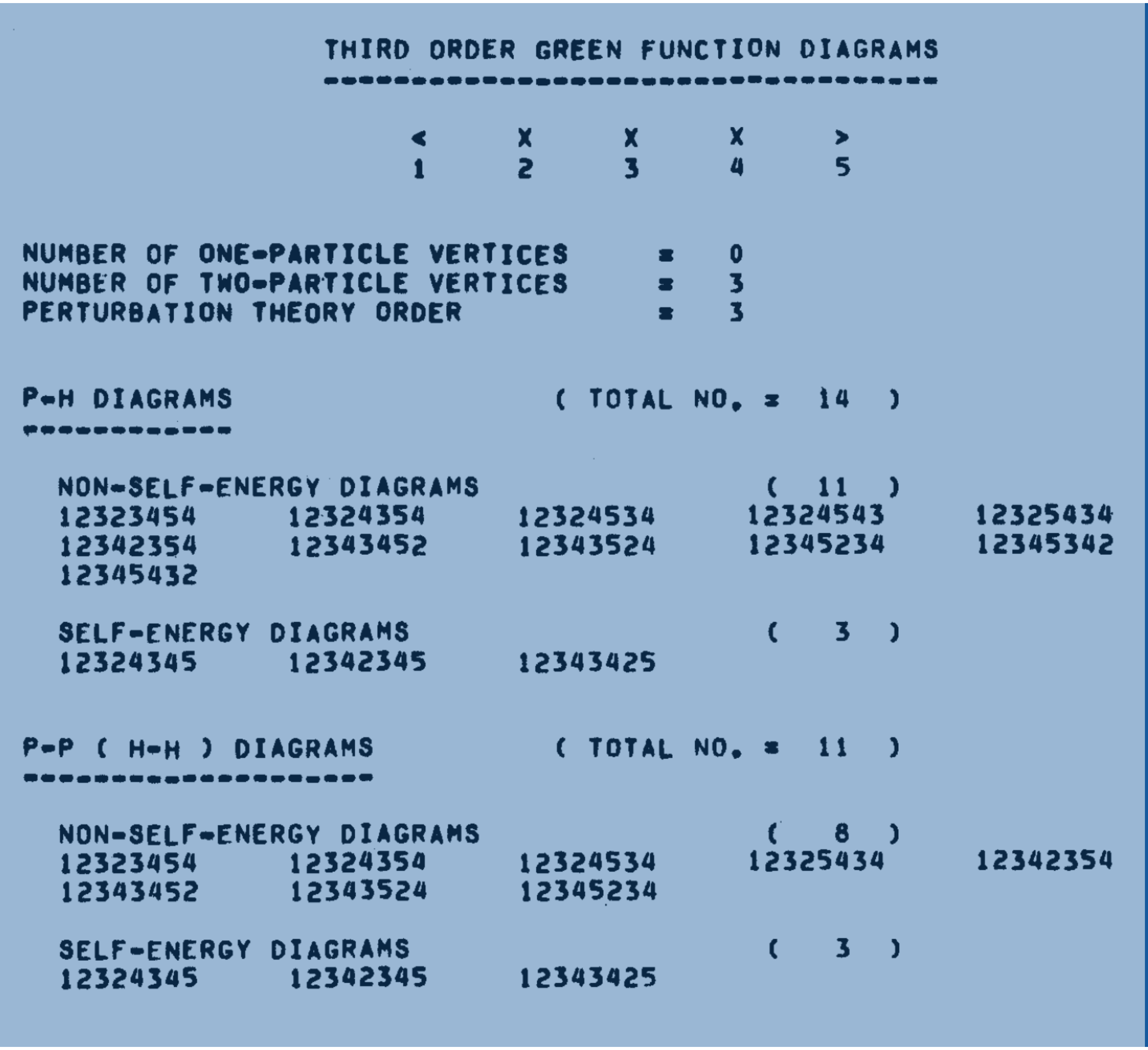


*Welcome to "Automated Tools for Many-Body Theory"*

*A Workshop of the Espace de Structure et de Réactions*
*Nucléaires Théorique*
*June 5–8, 2023*



```
                    THIRD ORDER GREEN FUNCTION DIAGRAMS
                    -----------------------------------

                         <     X     X     X     >
                         1     2     3     4     5

NUMBER OF ONE-PARTICLE VERTICES        =   0
NUMBER OF TWO-PARTICLE VERTICES        =   3
PERTURBATION THEORY ORDER              =   3

P-H DIAGRAMS                    ( TOTAL NO. =  14   )
------------

  NON-SELF-ENERGY DIAGRAMS                   (  11   )
  12323454     12324354     12324534     12324543     12325434
  12342354     12343452     12343524     12345234     12345342
  12345432

  SELF-ENERGY DIAGRAMS                       (   3   )
  12324345     12342345     12343425

P-P ( H-H ) DIAGRAMS            ( TOTAL NO. =  11   )
--------------------

  NON-SELF-ENERGY DIAGRAMS                   (   8   )
  12323454     12324354     12324534     12325434     12342354
  12343452     12343524     12345234

  SELF-ENERGY DIAGRAMS                       (   3   )
  12324345     12342345     12343425
```

# *An Introduction to the History of Computer-Aided Methods in Quantum Chemistry*

Francesco Evangelista
Emory University

Automated tools for many-body theory | Espace de Structure et de réactions Nucléaires Théorique | June 5, 2023

## *Workshop Goals*

1. To introduce attendants to different approaches to computer-aided derivation techniques for many-body theory,

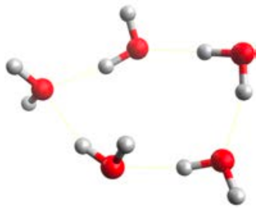
**2.** To exchange ideas regarding state-of-the-art automatic derivation methods between quantum chemists and nuclear physicists,

**3.** To discuss open problems in the field of automatic derivation, including the factorization of tensor contractions and identification of identical terms,

**4.** To identify ways to make current automatic derivation tools interoperable as a way to validate, benchmark, and expand the capabilities of current codes.

# *Quantum Chemistry: Computational Chemistry From First Principles*

**Water**



**Water molecules**

**Hamiltonian operator (fixed nuclei approximation)**

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i V(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

**Kinetic energy of electrons**

**Electron-nucleus attraction**

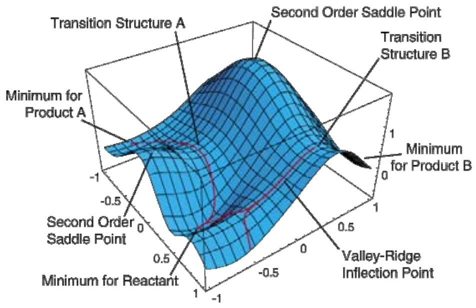
**Electron-electron repulsion**

## Time-independent Schrödinger equation

**Energy levels, potential energy surface**

$$\hat{H}\Psi(\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{R})$$

**Energy as a function of nuclear coordinates (R)**



## Time-dependent Schrödinger equation

**Dynamics (e.g., interaction with external fields)**

$$i\hbar\frac{\partial\Psi(\mathbf{R};t)}{\partial t} = \hat{H}\Psi(\mathbf{R};t)$$

**Wave function at time *t***

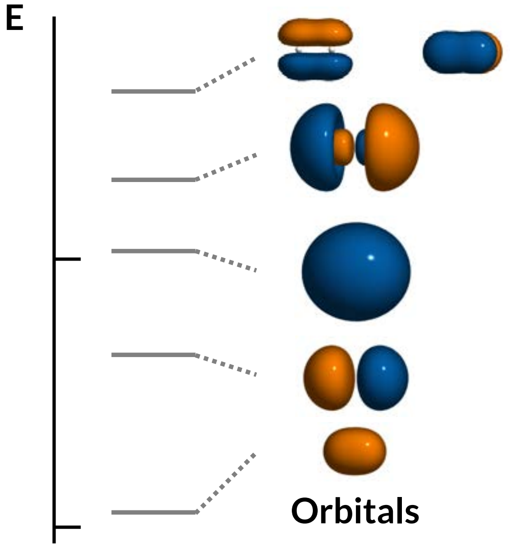
# *The Electron Correlation Problem*

The electronic wave function is a complex highly-dimensional object

$$\mathbf{x}_i = ( \underbrace{\mathbf{r}_i}_{\text{position}} , \underbrace{\sigma_i}_{\text{spin}} )$$

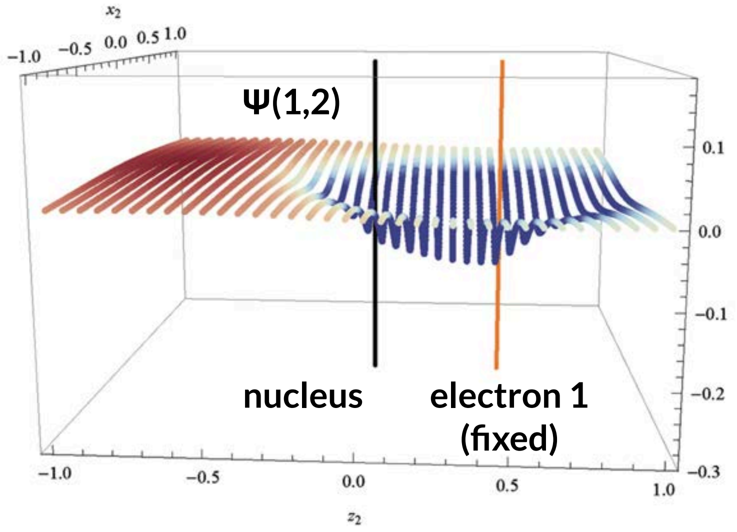
**One electron**

$$\Psi(\mathbf{x}_1)$$



***N* electrons**

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$



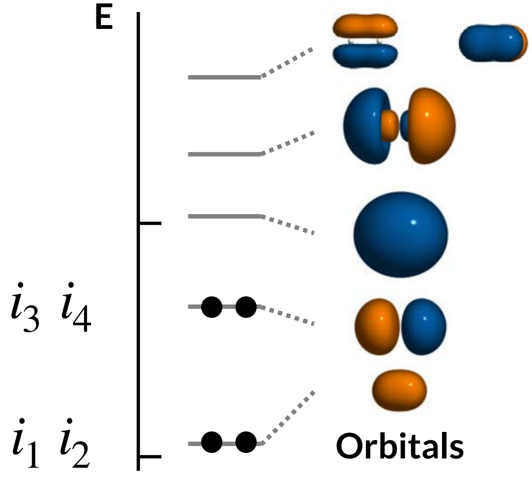
# *Chemistry and the Electron Correlation Problem*

The wave function is a linear combination of all arrangements of electrons in a set of orbitals (Slater determinants)

$$|\Psi\rangle = \sum_{I} C_I |\Phi_I\rangle = \sum_{i_1<i_2<\ldots<i_N}^{K} C_{i_1 i_2 \cdots i_N} |\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N}\rangle$$

**Slater determinant**

**Coefficient of a Slater determinant (unknown)**



# Chemistry and the Electron Correlation Problem

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$$|\Psi\rangle = \sum_{I} C_I |\Phi_I\rangle = \sum_{i_1<i_2<\ldots<i_N}^{K} C_{i_1 i_2 \cdots i_N} |\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N}\rangle$$

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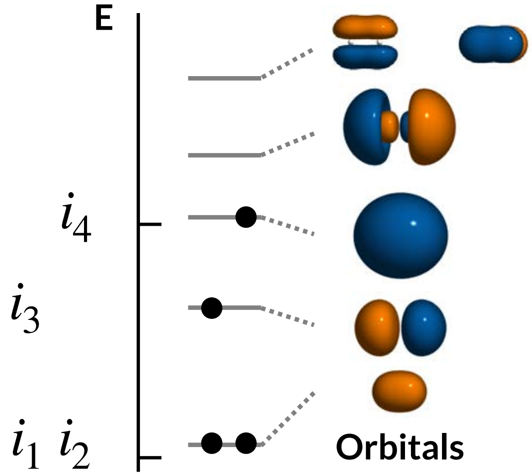

# Chemistry and the Electron Correlation Problem

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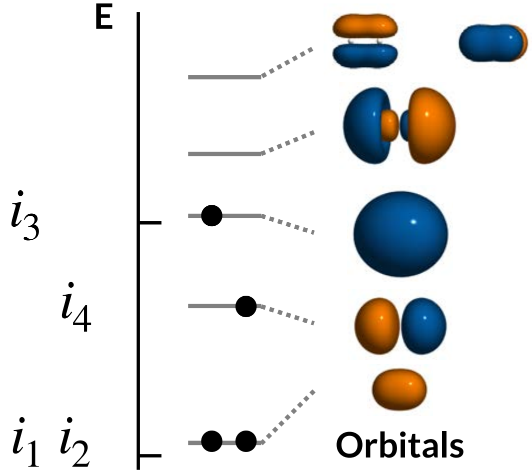
**Slater determinant**

**Coefficient of a Slater determinant (unknown)**



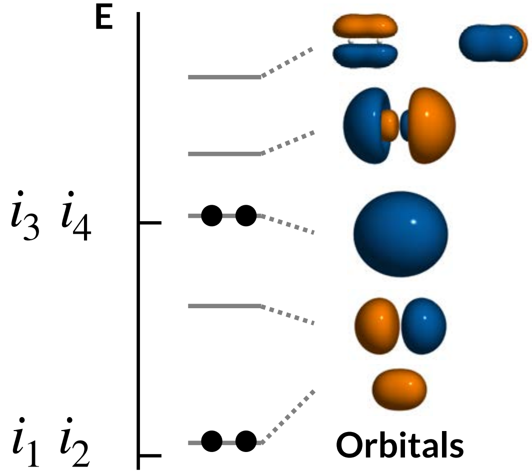
# ***Chemistry and the Electron Correlation Problem***

The wave function is a linear combination of all arrangements of electrons in a set of orbitals (Slater determinants)

$$|\Psi\rangle = \sum_I C_I|\Phi_I\rangle = \sum_{i_1<i_2<\ldots<i_N}^{K} C_{i_1 i_2\cdots i_N}|\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N}\rangle$$

**Slater determinant**

**Coefficient of a Slater determinant (unknown)**



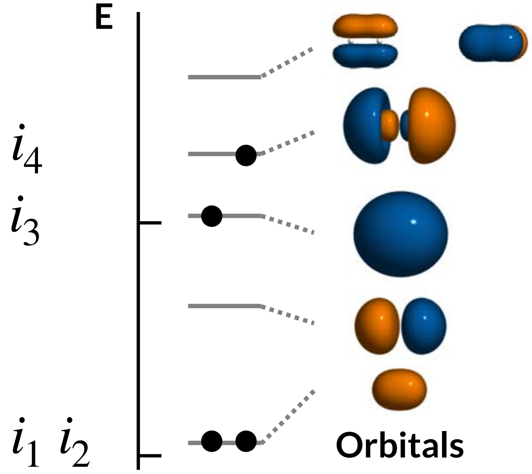
# Chemistry and the Electron Correlation Problem

The wave function is a linear combination of all arrangements of electrons in a set of orbitals (Slater determinants)

$$|\Psi\rangle = \sum_I C_I |\Phi_I\rangle = \sum_{i_1<i_2<\ldots<i_N}^{K} C_{i_1 i_2 \cdots i_N} \, |\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N}\rangle$$

**Slater determinant**

**Coefficient of a Slater determinant (unknown)**



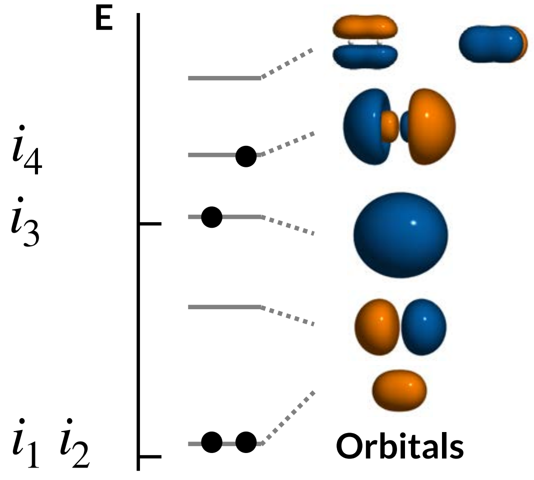
# Chemistry and the Electron Correlation Problem

The wave function is a linear combination of all arrangements of electrons in a set of orbitals (Slater determinants)

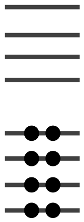
$$|\Psi\rangle = \sum_I C_I |\Phi_I\rangle = \sum_{i_1<i_2<\ldots<i_N}^{K} C_{i_1 i_2 \cdots i_N} |\varphi_{i_1}\varphi_{i_2}\ldots\varphi_{i_N}\rangle$$

**Slater determinant**

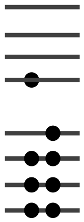
**Coefficient of a Slater determinant (unknown)**



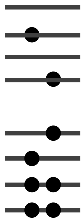
$$|\Psi\rangle = c_0 \qquad + c_S \qquad \ldots + c_D \qquad \ldots$$



**Mean field (MO picture)**



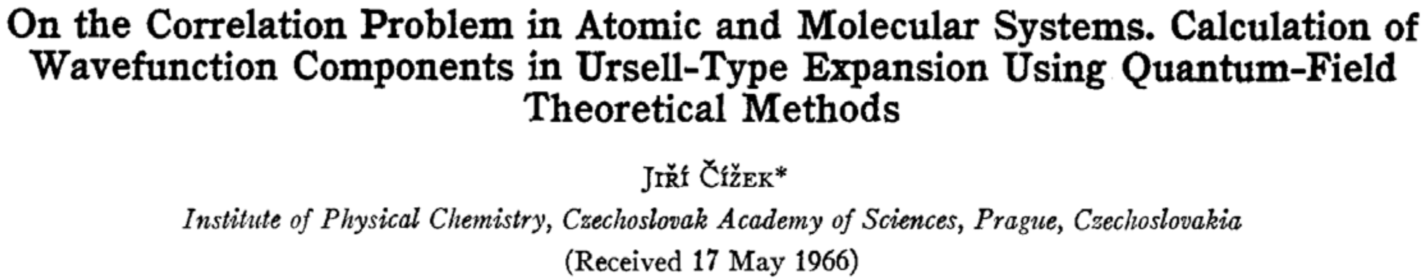
**Orbital relaxation**



**2-electron correlation**

$$\#\text{ of determinants} \propto \binom{K}{N}$$

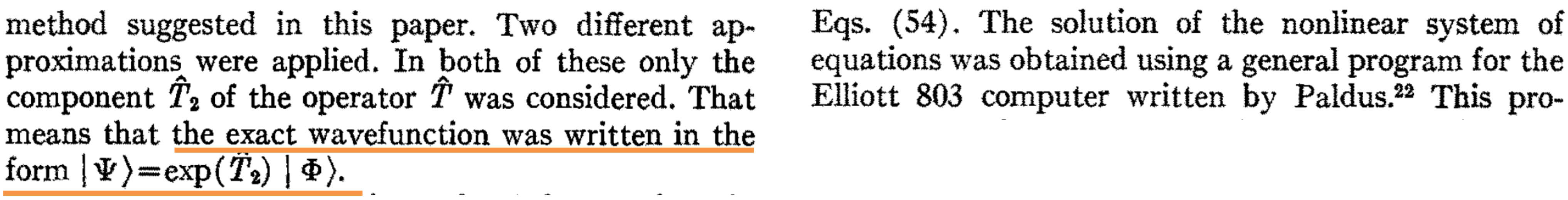
# Enter Many-Body Methods in Quantum Chemistry



### On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods

Jiří Čížek*
*Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia*

(Received 17 May 1966)



method suggested in this paper. Two different approximations were applied. In both of these only the component $\hat{T}_2$ of the operator $\hat{T}$ was considered. That means that the exact wavefunction was written in the form $|\Psi\rangle=\exp(\hat{T}_2)\,|\Phi\rangle$.

Eqs. (54). The solution of the nonlinear system of equations was obtained using a general program for the Elliott 803 computer written by Paldus.[22] This pro-

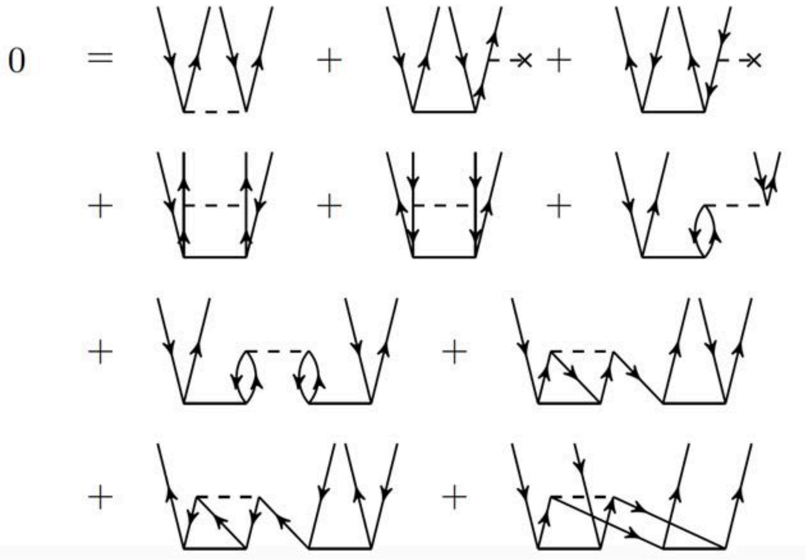
# *Computer-Aided Methods in Quantum Chemistry*

## Purposes of computer-aided development

- Automate the derivation and implementation of theories that lead to equations that are too complicated to be handled by a human

- Provide reference values for the implementation of new methods.

- Quickly explore new theoretical methods that otherwise would take too long to code and

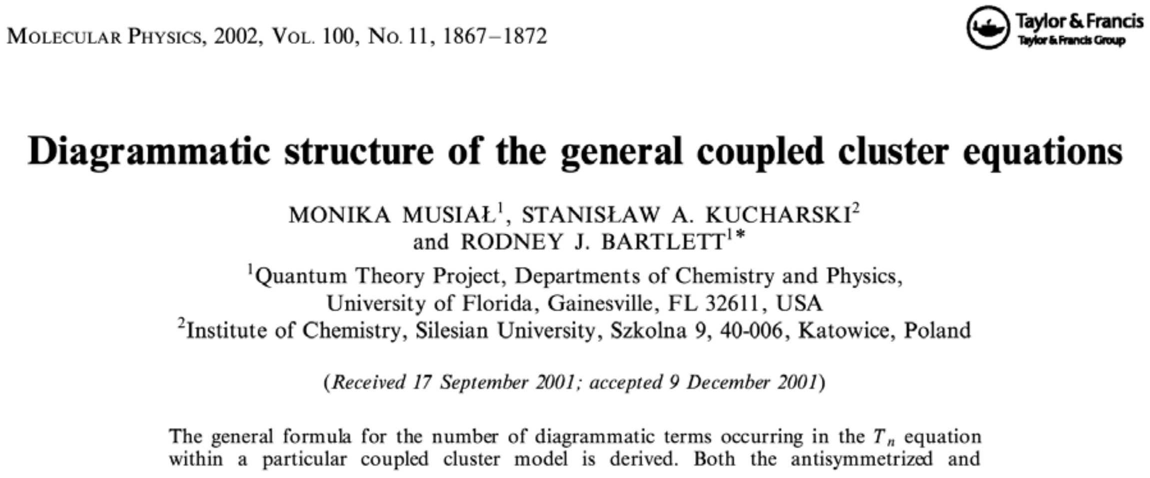


# Counting Diagrams in Coupled-Cluster Theory

$$\langle \Phi_{ij\cdots}^{ab\cdots} | e^{-T} H e^{T} | \Phi \rangle = \langle \Phi_{ij\cdots}^{ab\cdots} | (H e^{T})_{\mathrm{conn}} | \Phi \rangle$$

$$| \Phi_{ij\cdots}^{ab\cdots} \rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \cdots \hat{a}_j \hat{a}_i | \Phi \rangle$$

$$T \approx T_1 + T_2 + \ldots T_n$$



MOLECULAR PHYSICS, 2002, VOL. 100, NO. 11, 1867–1872

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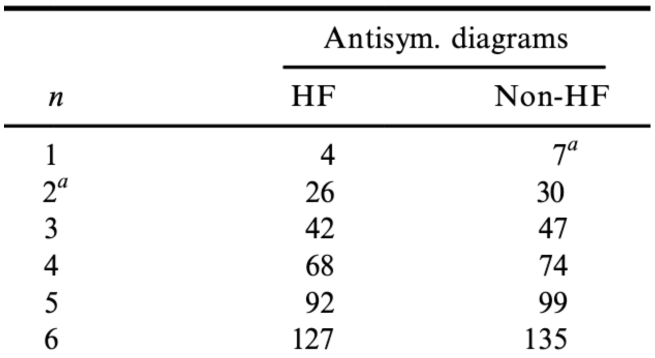
## Diagrammatic structure of the general coupled cluster equations

MONIKA MUSIAŁ[1], STANISŁAW A. KUCHARSKI[2]
and RODNEY J. BARTLETT[1]*
[1]Quantum Theory Project, Departments of Chemistry and Physics,
University of Florida, Gainesville, FL 32611, USA
[2]Institute of Chemistry, Silesian University, Szkolna 9, 40-006, Katowice, Poland

(*Received 17 September 2001; accepted 9 December 2001*)

The general formula for the number of diagrammatic terms occurring in the $T_n$ equation within a particular coupled cluster model is derived. Both the antisymmetrized and

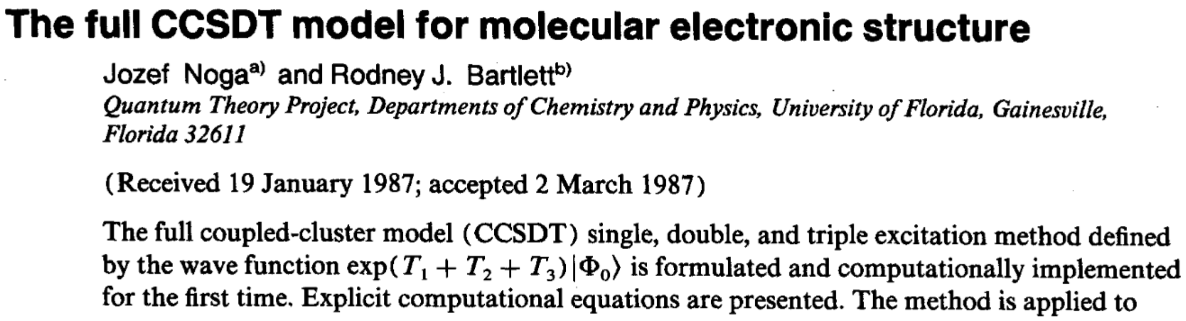
For $T$ truncated to order $n$, the number of diagrams grows as $n^3$



| | Antisym. diagrams | |
|---|---|---|
| $n$ | HF | Non-HF |
| 1 | 4 | $7^a$ |
| $2^a$ | 26 | 30 |
| 3 | 42 | 47 |
| 4 | 68 | 74 |
| 5 | 92 | 99 |
| 6 | 127 | 135 |

1.Musiał, M., Kucharski, S. A. & Bartlett, R. J. *J. Chem. Phys.* **116**, 4382 (2002).

# The First CCSDT Results Were Slightly Incorrect

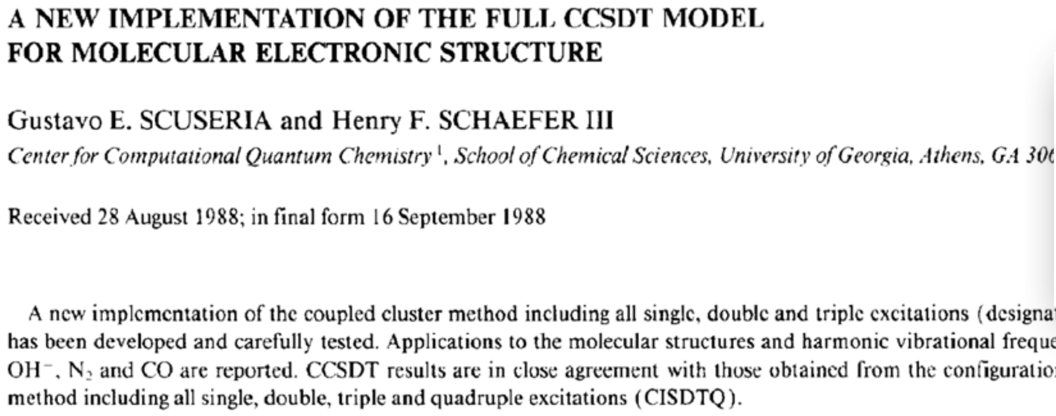


## The full CCSDT model for molecular electronic structure

Jozef Noga[a] and Rodney J. Bartlett[b]
*Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611*

(Received 19 January 1987; accepted 2 March 1987)

The full coupled-cluster model (CCSDT) single, double, and triple excitation method defined by the wave function $\exp(T_1 + T_2 + T_3)|\Phi_0\rangle$ is formulated and computationally implemented for the first time. Explicit computational equations are presented. The method is applied to

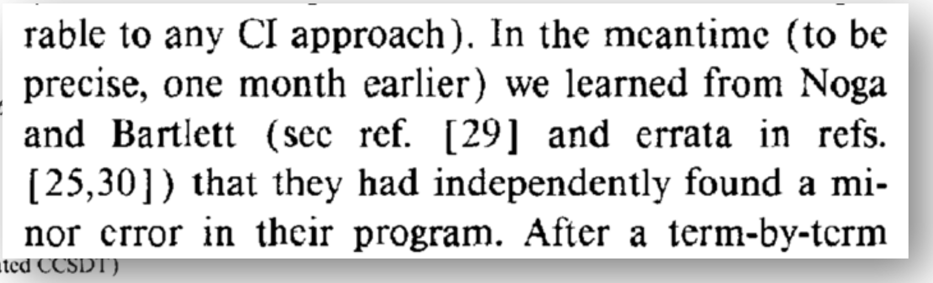


## A NEW IMPLEMENTATION OF THE FULL CCSDT MODEL FOR MOLECULAR ELECTRONIC STRUCTURE

Gustavo E. SCUSERIA and Henry F. SCHAEFER III
*Center for Computational Quantum Chemistry* [1], *School of Chemical Sciences, University of Georgia, Athens, GA 30*

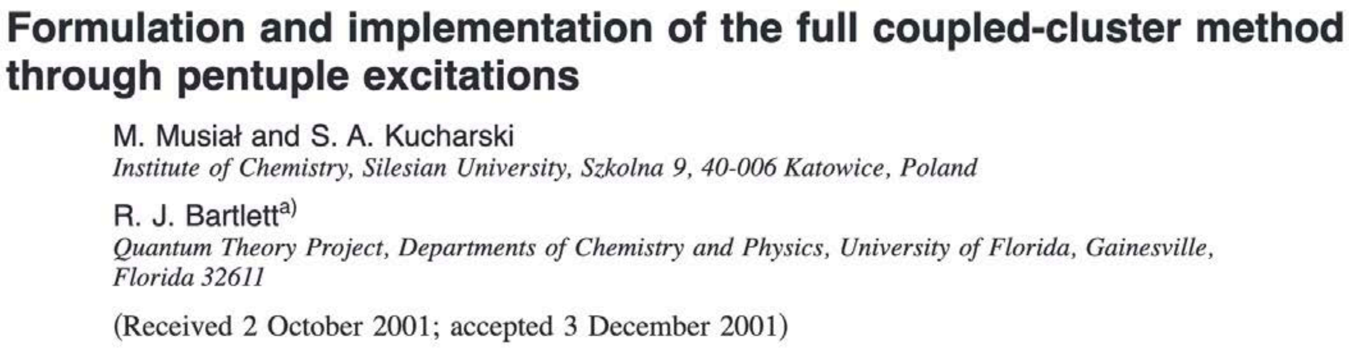
Received 28 August 1988; in final form 16 September 1988

A new implementation of the coupled cluster method including all single, double and triple excitations (designated CCSDT) has been developed and carefully tested. Applications to the molecular structures and harmonic vibrational frequencies of HF, $OH^-$, $N_2$ and CO are reported. CCSDT results are in close agreement with those obtained from the configuration interaction method including all single, double, triple and quadruple excitations (CISDTQ).



rable to any CI approach). In the meantime (to be precise, one month earlier) we learned from Noga and Bartlett (see ref. [29] and errata in refs. [25,30]) that they had independently found a minor error in their program. After a term-by-term

# CCSDTQP Implementation (Human)



## Formulation and implementation of the full coupled-cluster method through pentuple excitations

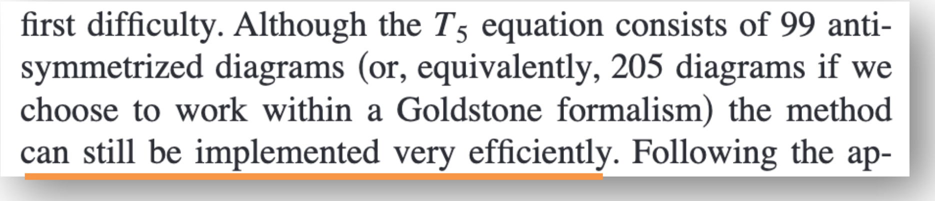
M. Musiał and S. A. Kucharski
*Institute of Chemistry, Silesian University, Szkolna 9, 40-006 Katowice, Poland*

R. J. Bartlett[a)]
*Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611*

(Received 2 October 2001; accepted 3 December 2001)

$$|\Psi_{\mathrm{CCSDTQP}}\rangle = e^{T_1+T_2+\ldots+T_5}|\Phi\rangle$$

This is the highest-level CC approximation ever implemented by hand



first difficulty. Although the $T_5$ equation consists of 99 antisymmetrized diagrams (or, equivalently, 205 diagrams if we choose to work within a Goldstone formalism) the method can still be implemented very efficiently. Following the ap-

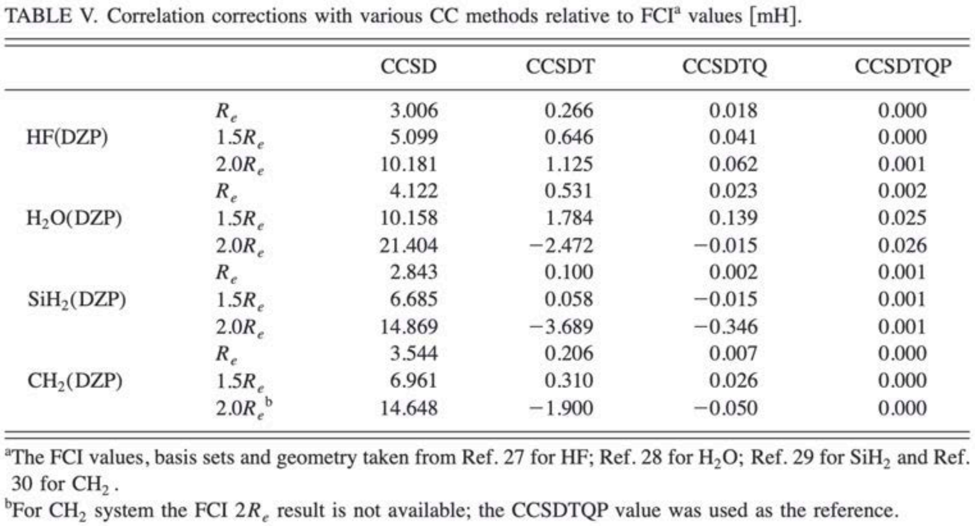


TABLE V. Correlation corrections with various CC methods relative to FCI[a] values [mH].

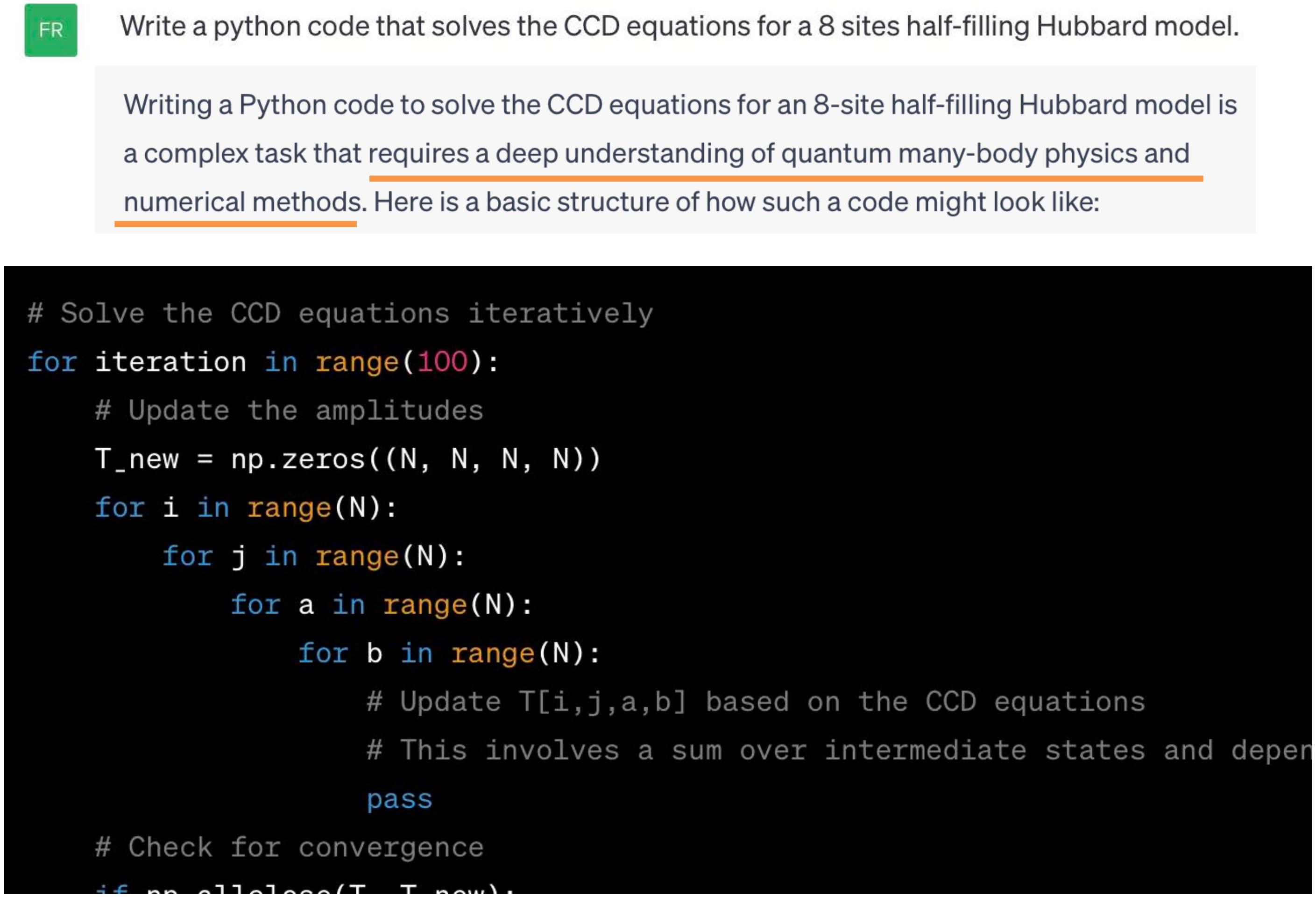
| | | CCSD | CCSDT | CCSDTQ | CCSDTQP |
|---|---|---|---|---|---|
| HF(DZP) | $R_e$ | 3.006 | 0.266 | 0.018 | 0.000 |
| | $1.5R_e$ | 5.099 | 0.646 | 0.041 | 0.000 |
| | $2.0R_e$ | 10.181 | 1.125 | 0.062 | 0.001 |
| $H_2O$(DZP) | $R_e$ | 4.122 | 0.531 | 0.023 | 0.002 |
| | $1.5R_e$ | 10.158 | 1.784 | 0.139 | 0.025 |
| | $2.0R_e$ | 21.404 | −2.472 | −0.015 | 0.026 |
| $SiH_2$(DZP) | $R_e$ | 2.843 | 0.100 | 0.002 | 0.001 |
| | $1.5R_e$ | 6.685 | 0.058 | −0.015 | 0.001 |
| | $2.0R_e$ | 14.869 | −3.689 | −0.346 | 0.001 |
| $CH_2$(DZP) | $R_e$ | 3.544 | 0.206 | 0.007 | 0.000 |
| | $1.5R_e$ | 6.961 | 0.310 | 0.026 | 0.000 |
| | $2.0R_e$[b] | 14.648 | −1.900 | −0.050 | 0.000 |

[a] The FCI values, basis sets and geometry taken from Ref. 27 for HF; Ref. 28 for $H_2O$; Ref. 29 for $SiH_2$ and Ref. 30 for $CH_2$.

[b] For $CH_2$ system the FCI $2R_e$ result is not available; the CCSDTQP value was used as the reference.

Musiał, M., Kucharski, S. A. & Bartlett, R. J. *J Chem Phys* **116**, 4382–4388 (2002).

# We're in 2023, Why Can't We Just Ask ChatGPT To Do It?



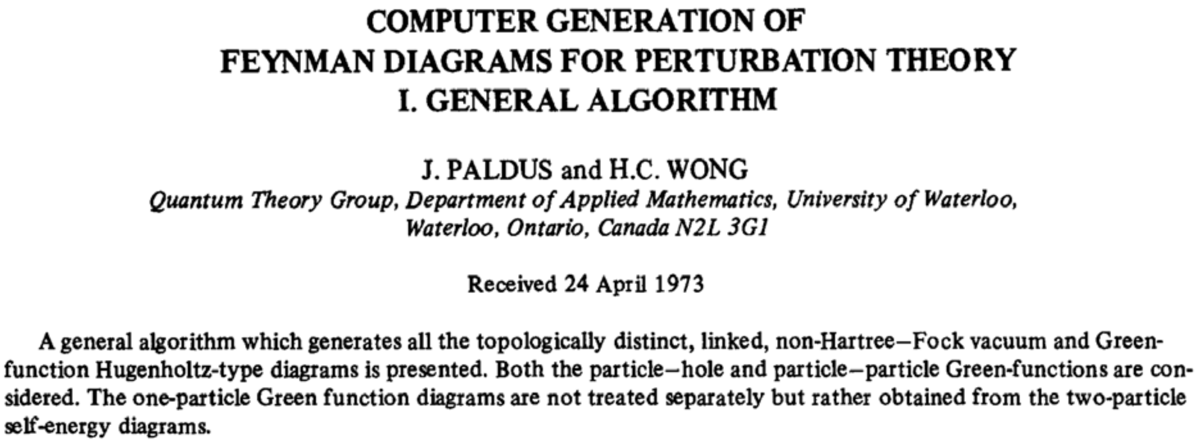
Write a python code that solves the CCD equations for a 8 sites half-filling Hubbard model.

Writing a Python code to solve the CCD equations for an 8-site half-filling Hubbard model is a complex task that requires a deep understanding of quantum many-body physics and numerical methods. Here is a basic structure of how such a code might look like:

```
# Solve the CCD equations iteratively
for iteration in range(100):
    # Update the amplitudes
    T_new = np.zeros((N, N, N, N))
    for i in range(N):
        for j in range(N):
            for a in range(N):
                for b in range(N):
                    # Update T[i,j,a,b] based on the CCD equations
                    # This involves a sum over intermediate states and depen
                    pass
    # Check for convergence
    if np.allclose(T, T_new):
```

# *Early History of Computer-Aided Quantum Chemistry*

# *1973: Paldus And Wong*

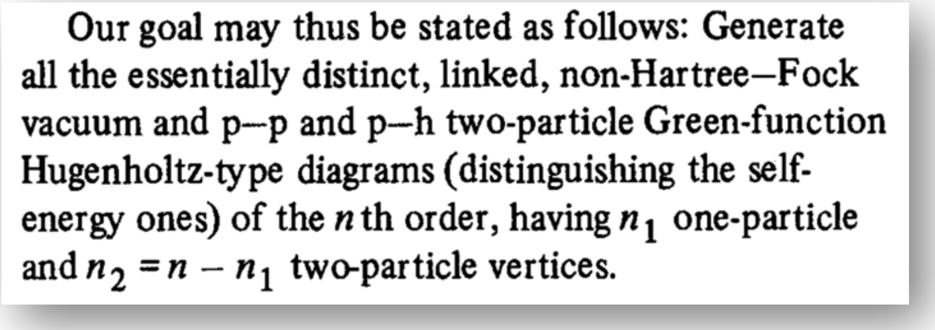


COMPUTER GENERATION OF
FEYNMAN DIAGRAMS FOR PERTURBATION THEORY
I. GENERAL ALGORITHM

J. PALDUS and H.C. WONG
*Quantum Theory Group, Department of Applied Mathematics, University of Waterloo,*
*Waterloo, Ontario, Canada N2L 3G1*

Received 24 April 1973

A general algorithm which generates all the topologically distinct, linked, non-Hartree–Fock vacuum and Green-function Hugenholtz-type diagrams is presented. Both the particle–hole and particle–particle Green-functions are considered. The one-particle Green function diagrams are not treated separately but rather obtained from the two-particle self-energy diagrams.



Our goal may thus be stated as follows: Generate all the essentially distinct, linked, non-Hartree–Fock vacuum and p–p and p–h two-particle Green-function Hugenholtz-type diagrams (distinguishing the self-energy ones) of the $n$th order, having $n_1$ one-particle and $n_2 = n - n_1$ two-particle vertices.

Based on Hugenholtz diagrams

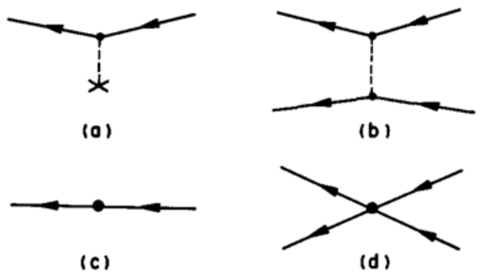


Fig. 1. One (a) and two (b) particle interaction vertices of the Goldstone type, representing the one- and two-particle parts of our hamiltonian (or of the hamiltonian of the perturbation), respectively. The Hugenholtz (degenerate) form of these vertices is shown, correspondingly, in (c) and (d).

**Goldstone** **Hugenholtz**

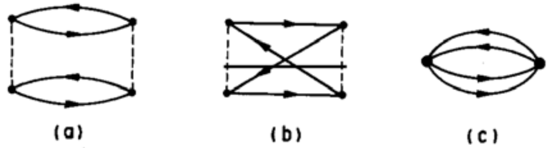


Fig. 2. Second order vacuum diagrams (a, b) in the Goldstone form and Hugenholtz (c) form, considering only two-particle interactions.

# 1973: Paldus and Wong

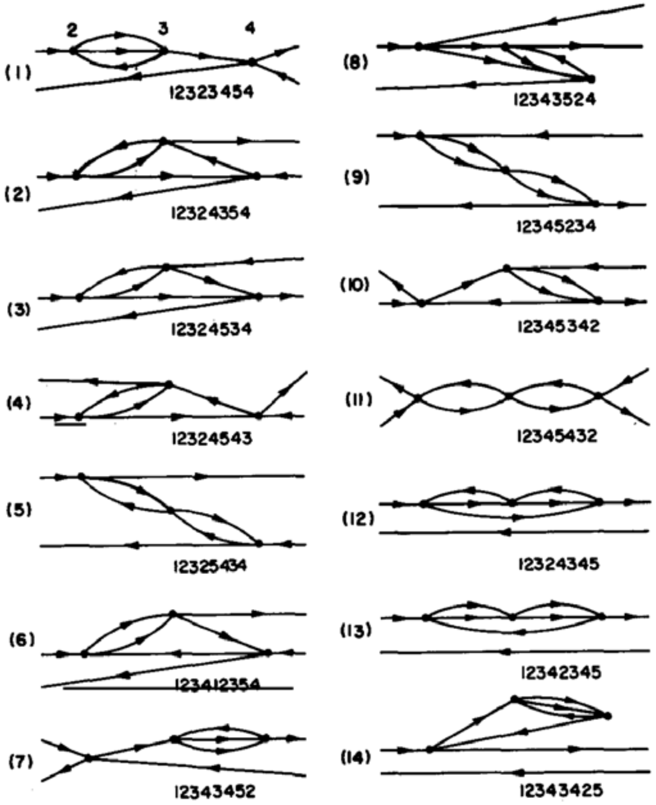


Fig. 5. Third order particle–hole Green-function diagrams generated in the second test case (INDEX = 1, N1 = 0, N2 = 3). The last three diagrams (12, 13, 14) are the self-energy diagrams. The "external" vertices (1 and 5 in this case) are "removed to infinity", thus giving the diagrmas its usual form. For other conventions see the caption to fig. 2.

# 1973: Paldus And Wong

A diagram is represented by a string. This is not a unique representation.

Two representations of the same diagram

$$S_1 = 12453243$$

$$S_2 = 12432453$$

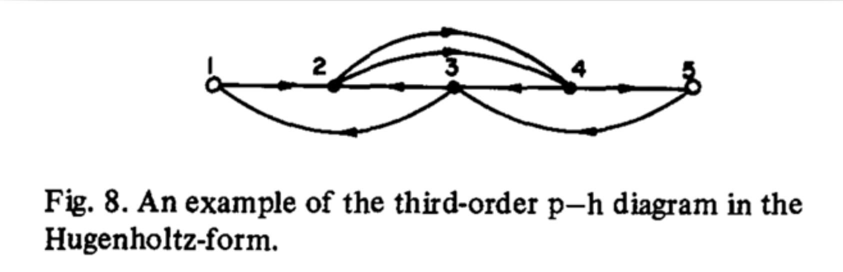
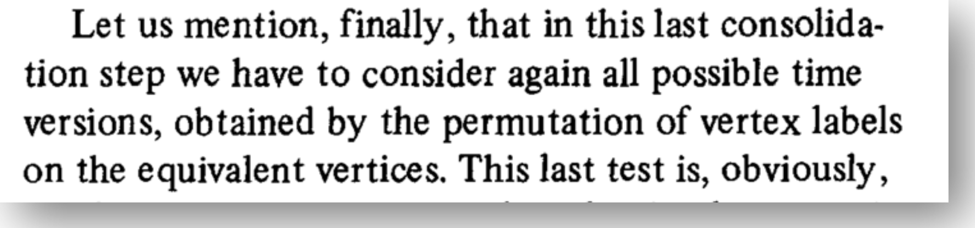


Fig. 8. An example of the third-order p–h diagram in the Hugenholtz-form.

Diagram consolidation was necessary to recognize topologically equivalent diagrams

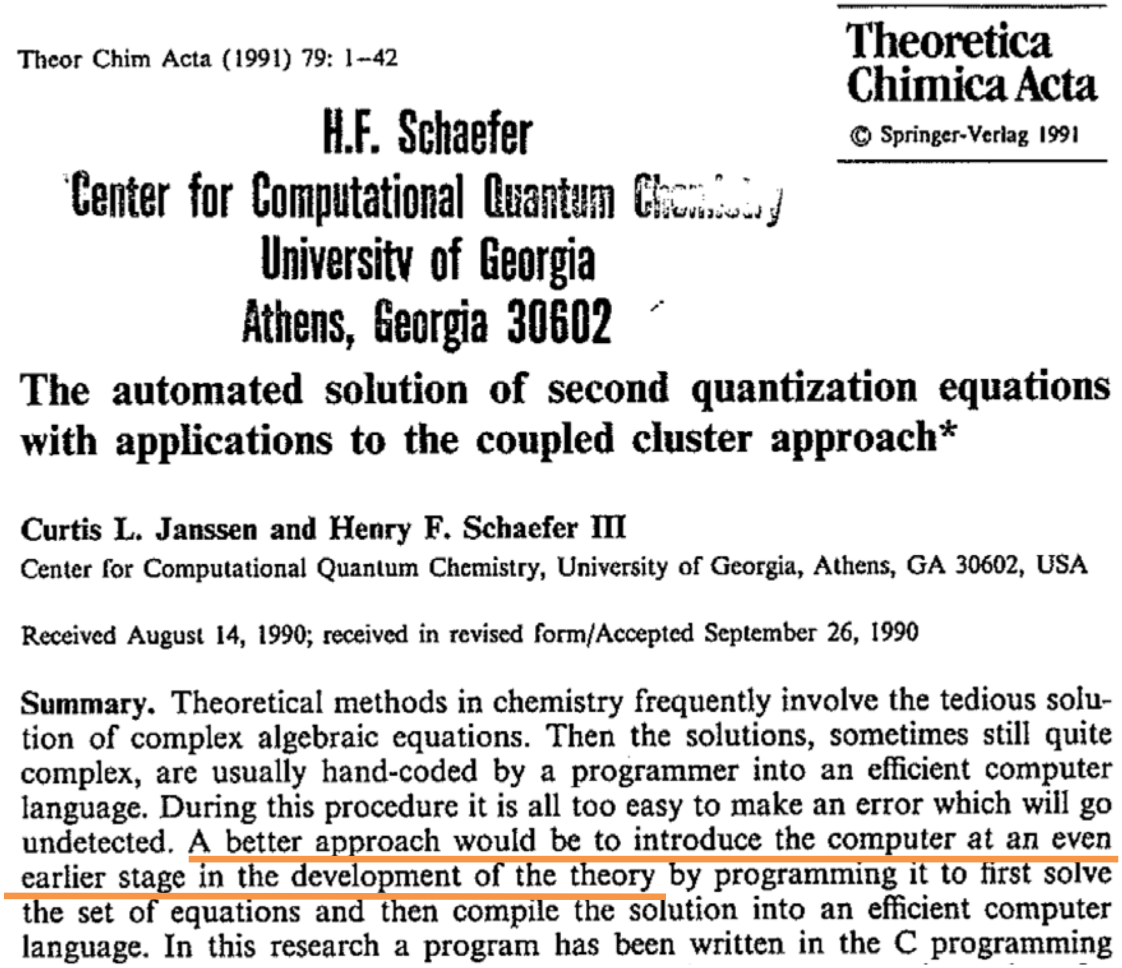
Paldus and Wong used adjacency matrices

$$S_1, S_2 \rightarrow \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$



Let us mention, finally, that in this last consolidation step we have to consider again all possible time versions, obtained by the permutation of vertex labels on the equivalent vertices. This last test is, obviously,

# 1991: Janssen and Schaefer



Theor Chim Acta (1991) 79: 1–42

Theoretica Chimica Acta
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H.F. Schaefer
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Athens, Georgia 30602

## The automated solution of second quantization equations with applications to the coupled cluster approach*

**Curtis L. Janssen and Henry F. Schaefer III**
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Received August 14, 1990; received in revised form/Accepted September 26, 1990

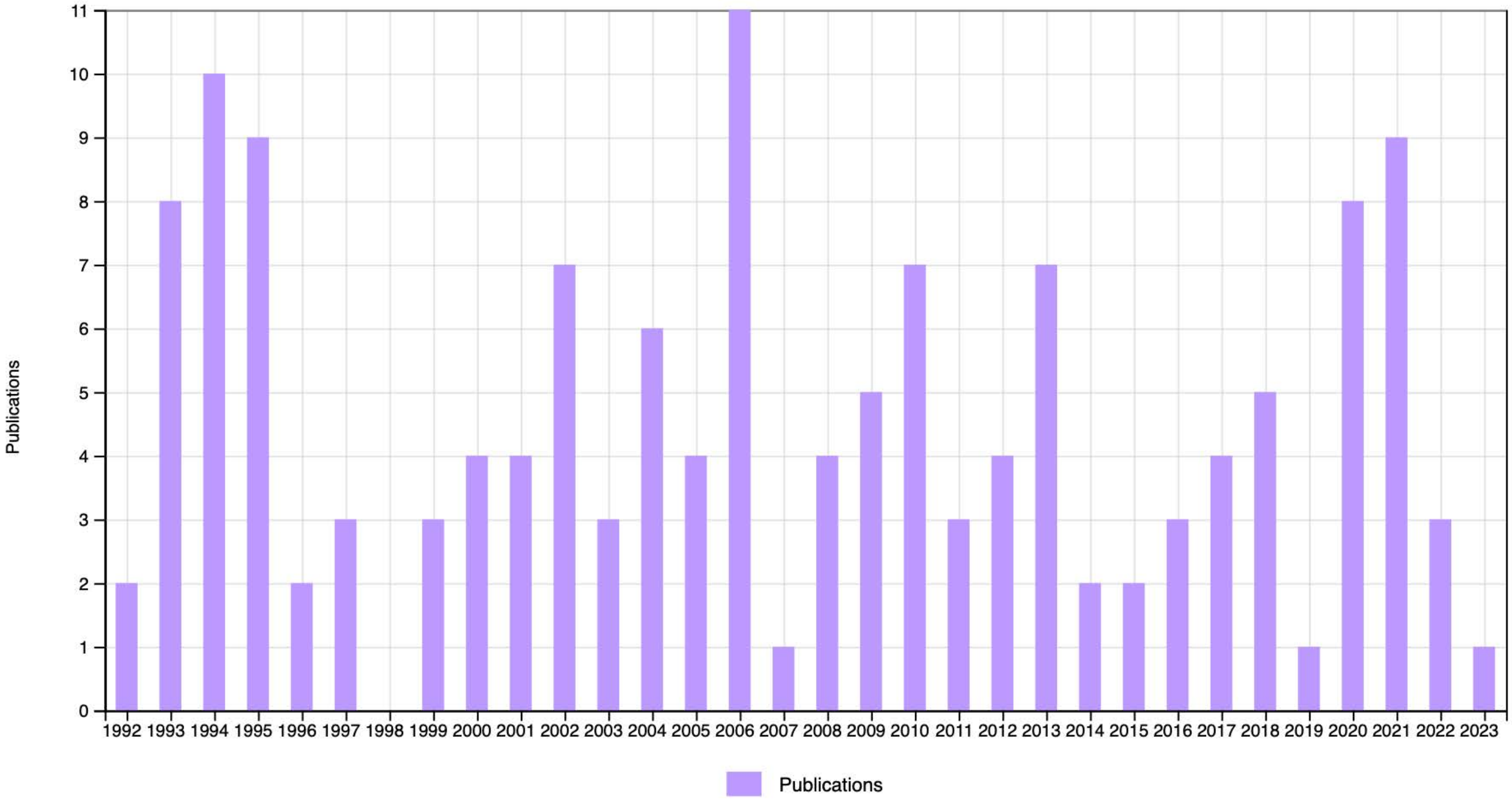
**Summary.** Theoretical methods in chemistry frequently involve the tedious solution of complex algebraic equations. Then the solutions, sometimes still quite complex, are usually hand-coded by a programmer into an efficient computer language. During this procedure it is all too easy to make an error which will go undetected. A better approach would be to introduce the computer at an even earlier stage in the development of the theory by programming it to first solve the set of equations and then compile the solution into an efficient computer language. In this research a program has been written in the C programming

Second quantization symbol manipulator (SQSYM).

A fundamental contribution to the field: This is the first example of a complete program (derivation + implementation).

## *1991: Janssen and Schaefer*

This paper was cited 145 times!

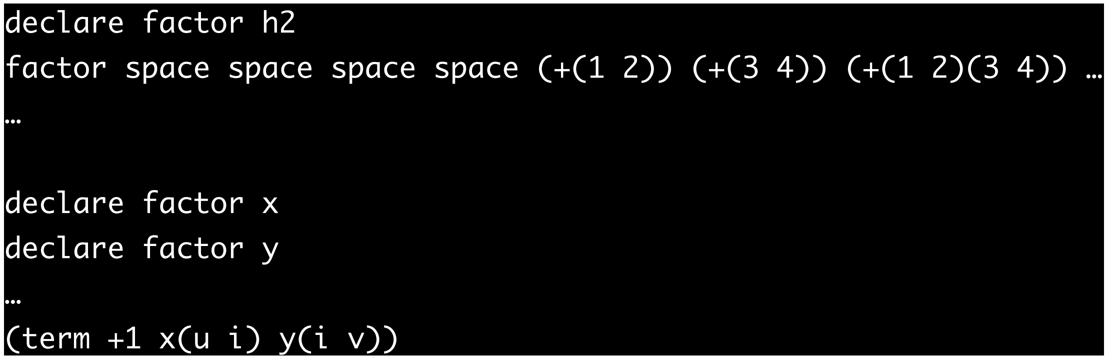


## *1991: Janssen and Schaefer*

SQSYM is actually two programs. The first one is an **interpreter + compiler**

**declare the two e integrals $(ij|kl)$**

**Build the expression for $\sum_i x_{ui} y_{iv}$**



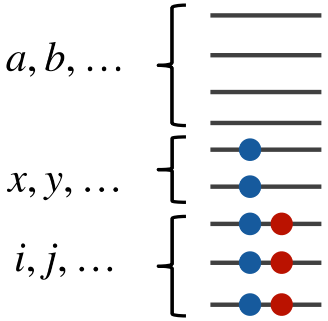
```
declare factor h2
factor space space space space (+(1 2)) (+(3 4)) (+(1 2)(3 4)) …
…

declare factor x
declare factor y
…
(term +1 x(u i) y(i v))
```

**Specify spaces of $(ij|kl)$ and the permutational symmetry**

The simplified expressions generated by SQSYM are then executed by the **correlation energy language** interpreter CORR

# 1991: Janssen and Schaefer

SQSYM was used to implement coupled cluster with singles and doubles (CCSD) for high-spin open-shell references



$$|\Psi\rangle = e^{T}|\Phi\rangle \qquad |\Phi\rangle = |\psi_1\psi_{\bar{1}}\cdots\psi_N\psi_{\bar{N}}\psi_{N+1}\cdots\psi_{N+M}\rangle$$

$$T = t_i^a\hat{E}_i^a + t_x^a\hat{E}_x^a + t_i^x\hat{E}_i^x + t_{ji}^{ba}\hat{E}_j^b\hat{E}_i^a + \ldots$$

In the HSOS case complications arise, so authors consider a partially spin-adapted variant

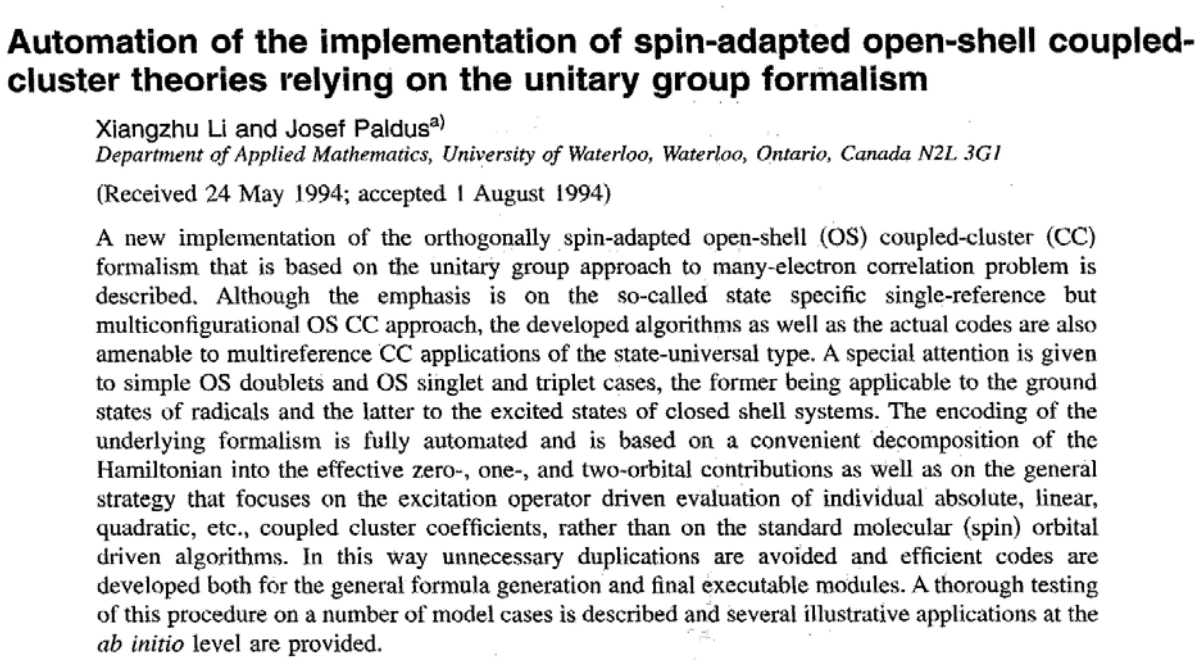
$$\bar{H} = e^{-T}He^{T} \neq (He^{T})_{\text{conn}}$$

New contractions are possible with a $T$ **on the left since** $t_x^a\hat{a}^\dagger_{a_\beta}\hat{a}_{x_\beta}$ destroys an unoccupied ($x$) spin orbital in $\Phi$

$$\bar{H} = \leftarrow \frac{1}{5!}[[[[[H,T]\cdots],T] + \ldots$$

Terms involving up to the eight power of $T$ enter into $\bar{H}$

# 1994: Li and Paldus



## Automation of the implementation of spin-adapted open-shell coupled-cluster theories relying on the unitary group formalism

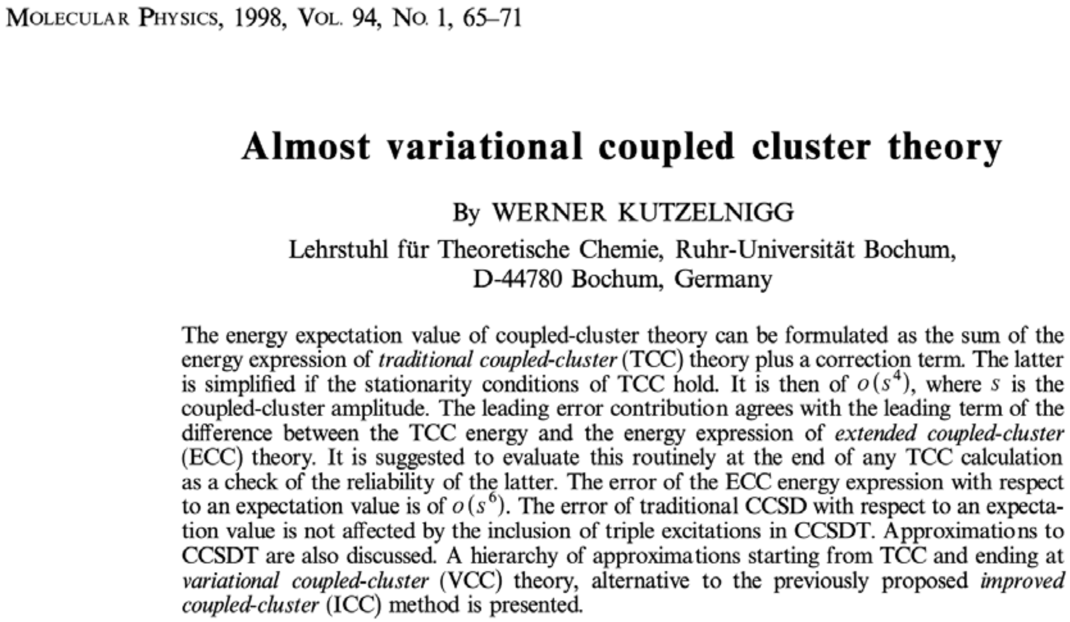
Xiangzhu Li and Josef Paldus[a)]
*Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

(Received 24 May 1994; accepted 1 August 1994)

A new implementation of the orthogonally spin-adapted open-shell (OS) coupled-cluster (CC) formalism that is based on the unitary group approach to many-electron correlation problem is described. Although the emphasis is on the so-called state specific single-reference but multiconfigurational OS CC approach, the developed algorithms as well as the actual codes are also amenable to multireference CC applications of the state-universal type. A special attention is given to simple OS doublets and OS singlet and triplet cases, the former being applicable to the ground states of radicals and the latter to the excited states of closed shell systems. The encoding of the underlying formalism is fully automated and is based on a convenient decomposition of the Hamiltonian into the effective zero-, one-, and two-orbital contributions as well as on the general strategy that focuses on the excitation operator driven evaluation of individual absolute, linear, quadratic, etc., coupled cluster coefficients, rather than on the standard molecular (spin) orbital driven algorithms. In this way unnecessary duplications are avoided and efficient codes are developed both for the general formula generation and final executable modules. A thorough testing of this procedure on a number of model cases is described and several illustrative applications at the *ab initio* level are provided.

# *Determinantal Methods*

# *1998: Kutzelnigg (Why Aren't We Doing More Benchmark Calculations?)*



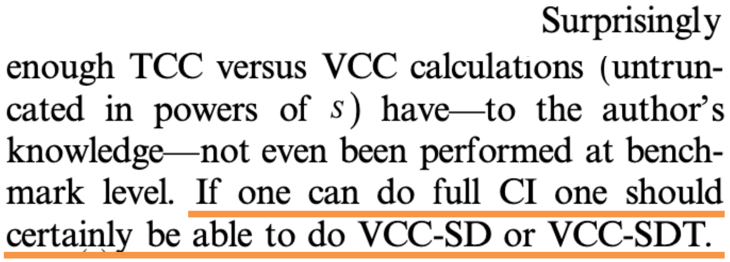
MOLECULAR PHYSICS, 1998, VOL. 94, NO. 1, 65–71

## Almost variational coupled cluster theory

By WERNER KUTZELNIGG

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum,
D-44780 Bochum, Germany

The energy expectation value of coupled-cluster theory can be formulated as the sum of the energy expression of *traditional coupled-cluster* (TCC) theory plus a correction term. The latter is simplified if the stationarity conditions of TCC hold. It is then of $o(s^4)$, where $s$ is the coupled-cluster amplitude. The leading error contribution agrees with the leading term of the difference between the TCC energy and the energy expression of *extended coupled-cluster* (ECC) theory. It is suggested to evaluate this routinely at the end of any TCC calculation as a check of the reliability of the latter. The error of the ECC energy expression with respect to an expectation value is of $o(s^6)$. The error of traditional CCSD with respect to an expectation value is not affected by the inclusion of triple excitations in CCSDT. Approximations to CCSDT are also discussed. A hierarchy of approximations starting from TCC and ending at *variational coupled-cluster* (VCC) theory, alternative to the previously proposed *improved coupled-cluster* (ICC) method is presented.



Surprisingly enough TCC versus VCC calculations (untruncated in powers of $s$) have—to the author's knowledge—not even been performed at benchmark level. If one can do full CI one should certainly be able to do VCC-SD or VCC-SDT.

If we can optimize FCI states with $|\Psi\rangle = \sum_I |\Phi_I\rangle c_I$, there is no reason we can't also benchmark coupled cluster methods by expanding $e^T|\Phi\rangle = \sum_I |\Phi_I\rangle c_I$

## How Do Determinant-Based Methods Work?

Express any state (vector) in the full configuration interaction determinant basis

$$|v\rangle = \sum_I |\Phi_I\rangle c_I \qquad c_I = (\mathbf{c})_I$$

The Hartree–Fock determinant

$$|\Phi\rangle \equiv |\Phi_0\rangle \qquad \mathbf{c} = (1,0,\ldots)$$

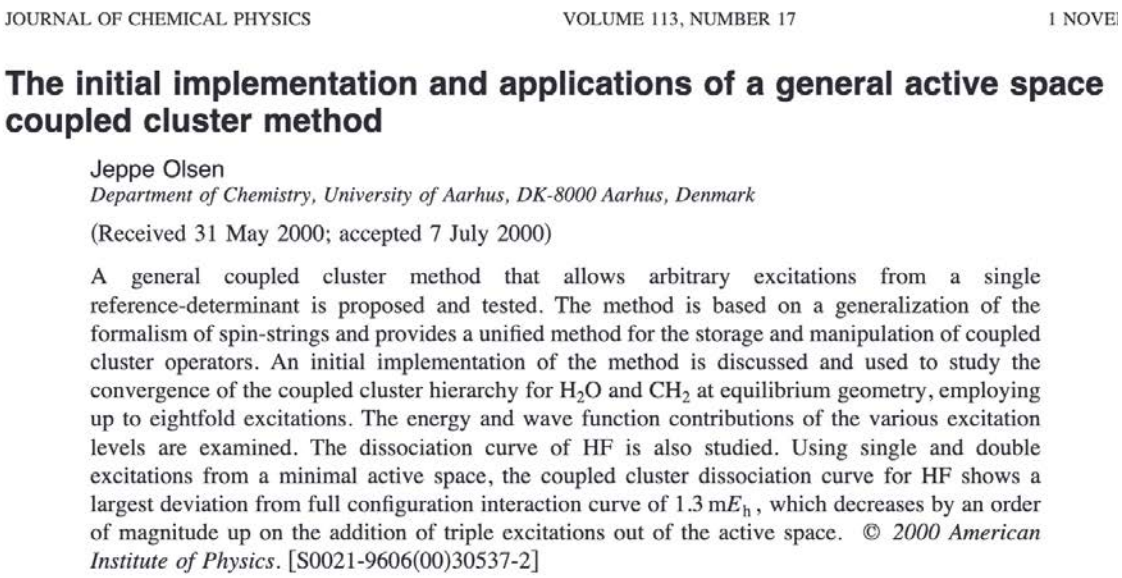
The coupled-cluster wave function

$e^T|\Phi_0\rangle$ $\quad\mathbf{c} = e^{\mathbf{T}}(1,0,\ldots)$ where $\mathbf{T}$ is the matrix representation of $T$ in the FCI basis

The Hamiltonian applied to the coupled-cluster wave function

$He^T|\Phi_0\rangle$ $\quad\mathbf{c} = \mathbf{H}e^{\mathbf{T}}(1,0,\ldots)$ one can re-use techniques developed for FCI (string-based)

# 2000: Olsen



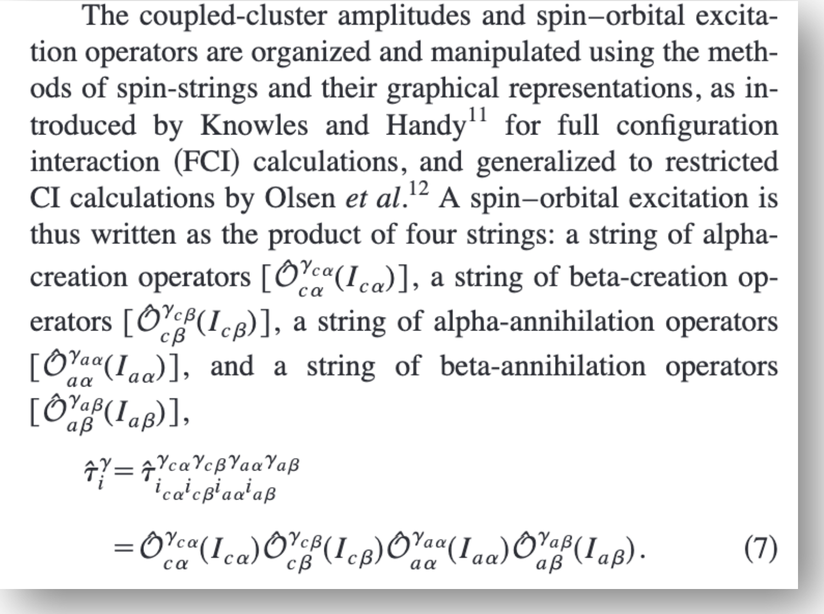
JOURNAL OF CHEMICAL PHYSICS VOLUME 113, NUMBER 17 1 NOVE

## The initial implementation and applications of a general active space coupled cluster method

Jeppe Olsen
*Department of Chemistry, University of Aarhus, DK-8000 Aarhus, Denmark*

(Received 31 May 2000; accepted 7 July 2000)

A general coupled cluster method that allows arbitrary excitations from a single reference-determinant is proposed and tested. The method is based on a generalization of the formalism of spin-strings and provides a unified method for the storage and manipulation of coupled cluster operators. An initial implementation of the method is discussed and used to study the convergence of the coupled cluster hierarchy for $H_2O$ and $CH_2$ at equilibrium geometry, employing up to eightfold excitations. The energy and wave function contributions of the various excitation levels are examined. The dissociation curve of HF is also studied. Using single and double excitations from a minimal active space, the coupled cluster dissociation curve for HF shows a largest deviation from full configuration interaction curve of 1.3 m$E_h$, which decreases by an order of magnitude up on the addition of triple excitations out of the active space. © *2000 American Institute of Physics*. [S0021-9606(00)30537-2]



The coupled-cluster amplitudes and spin–orbital excitation operators are organized and manipulated using the methods of spin-strings and their graphical representations, as introduced by Knowles and Handy[11] for full configuration interaction (FCI) calculations, and generalized to restricted CI calculations by Olsen *et al.*[12] A spin–orbital excitation is thus written as the product of four strings: a string of alpha-creation operators $[\hat{O}^{\gamma_{c\alpha}}_{c\alpha}(I_{c\alpha})]$, a string of beta-creation operators $[\hat{O}^{\gamma_{c\beta}}_{c\beta}(I_{c\beta})]$, a string of alpha-annihilation operators $[\hat{O}^{\gamma_{a\alpha}}_{a\alpha}(I_{a\alpha})]$, and a string of beta-annihilation operators $[\hat{O}^{\gamma_{a\beta}}_{a\beta}(I_{a\beta})]$,

$$\hat{\tau}^{\gamma}_{i} = \hat{\tau}^{\gamma_{c\alpha}\gamma_{c\beta}\gamma_{a\alpha}\gamma_{a\beta}}_{i_{c\alpha}i_{c\beta}i_{a\alpha}i_{a\beta}} = \hat{O}^{\gamma_{c\alpha}}_{c\alpha}(I_{c\alpha})\hat{O}^{\gamma_{c\beta}}_{c\beta}(I_{c\beta})\hat{O}^{\gamma_{a\alpha}}_{a\alpha}(I_{a\alpha})\hat{O}^{\gamma_{a\beta}}_{a\beta}(I_{a\beta}). \quad (7)$$

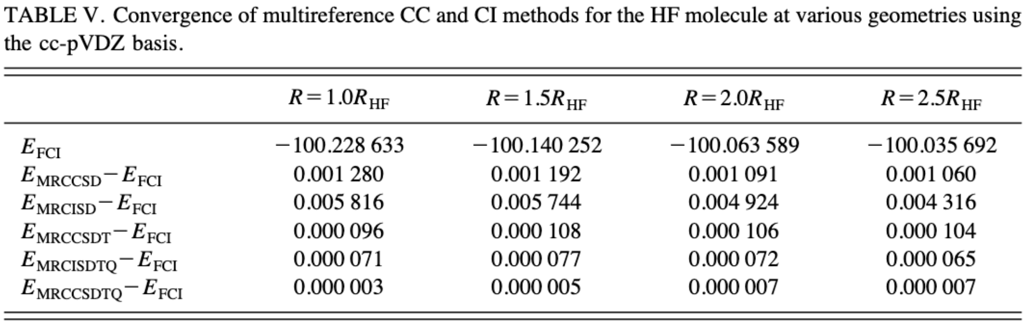
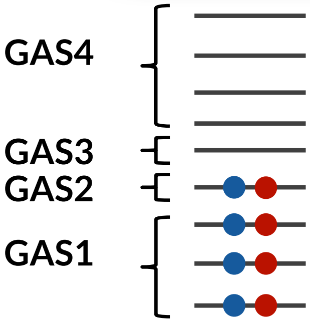


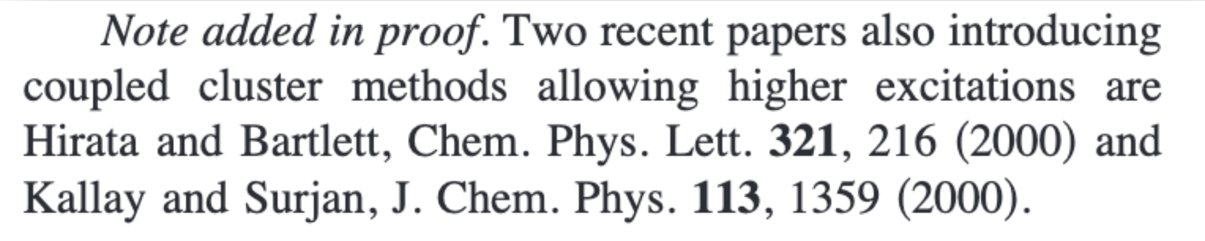
TABLE V. Convergence of multireference CC and CI methods for the HF molecule at various geometries using the cc-pVDZ basis.

| | $R=1.0R_{HF}$ | $R=1.5R_{HF}$ | $R=2.0R_{HF}$ | $R=2.5R_{HF}$ |
|---|---|---|---|---|
| $E_{FCI}$ | −100.228 633 | −100.140 252 | −100.063 589 | −100.035 692 |
| $E_{MRCCSD}-E_{FCI}$ | 0.001 280 | 0.001 192 | 0.001 091 | 0.001 060 |
| $E_{MRCISD}-E_{FCI}$ | 0.005 816 | 0.005 744 | 0.004 924 | 0.004 316 |
| $E_{MRCCSDT}-E_{FCI}$ | 0.000 096 | 0.000 108 | 0.000 106 | 0.000 104 |
| $E_{MRCISDTQ}-E_{FCI}$ | 0.000 071 | 0.000 077 | 0.000 072 | 0.000 065 |
| $E_{MRCCSDTQ}-E_{FCI}$ | 0.000 003 | 0.000 005 | 0.000 007 | 0.000 007 |



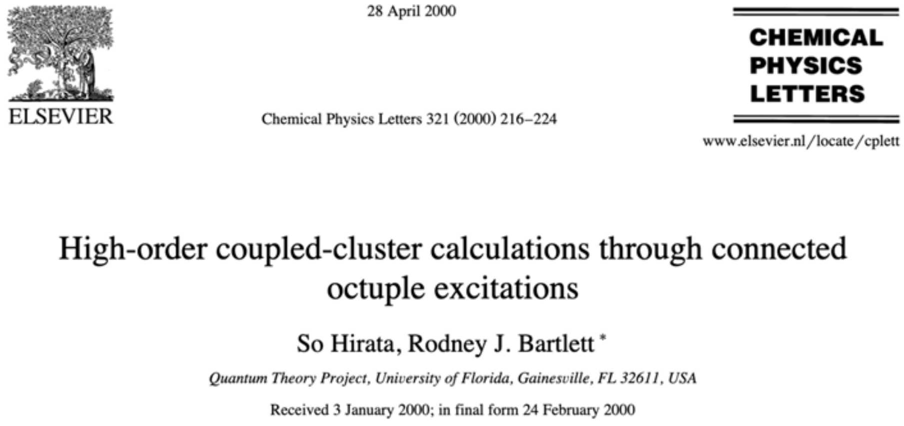
Choose $T$ such that
0–2 holes in GAS1
0–4 holes in GAS1 + GAS2
0–2 electrons in GAS4
0–4 holes in GAS3 + GAS4

# 2000: Olsen



*Note added in proof*. Two recent papers also introducing coupled cluster methods allowing higher excitations are Hirata and Bartlett, Chem. Phys. Lett. **321**, 216 (2000) and Kallay and Surjan, J. Chem. Phys. **113**, 1359 (2000).

# 2000: Hirata, Nooijen, Bartlett



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28 April 2000

Chemical Physics Letters 321 (2000) 216–224

CHEMICAL PHYSICS LETTERS

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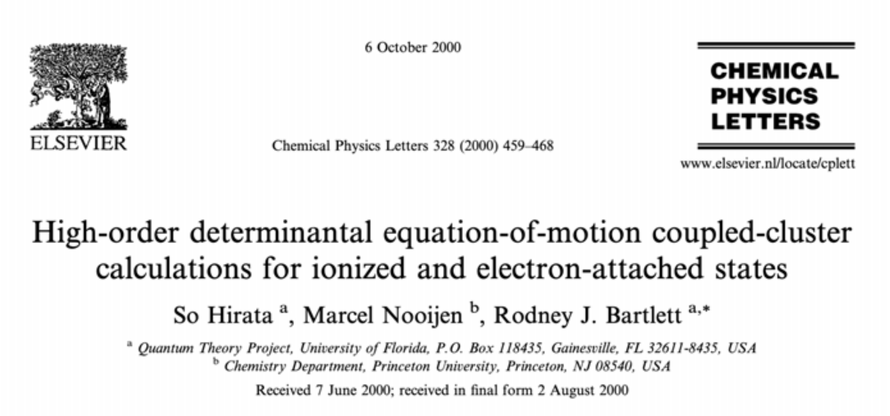
High-order coupled-cluster calculations through connected octuple excitations

So Hirata, Rodney J. Bartlett *

*Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA*

Received 3 January 2000; in final form 24 February 2000



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6 October 2000

Chemical Physics Letters 328 (2000) 459–468

CHEMICAL PHYSICS LETTERS

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High-order determinantal equation-of-motion coupled-cluster calculations for ionized and electron-attached states

So Hirata [a], Marcel Nooijen [b], Rodney J. Bartlett [a,*]

[a] *Quantum Theory Project, University of Florida, P.O. Box 118435, Gainesville, FL 32611-8435, USA*

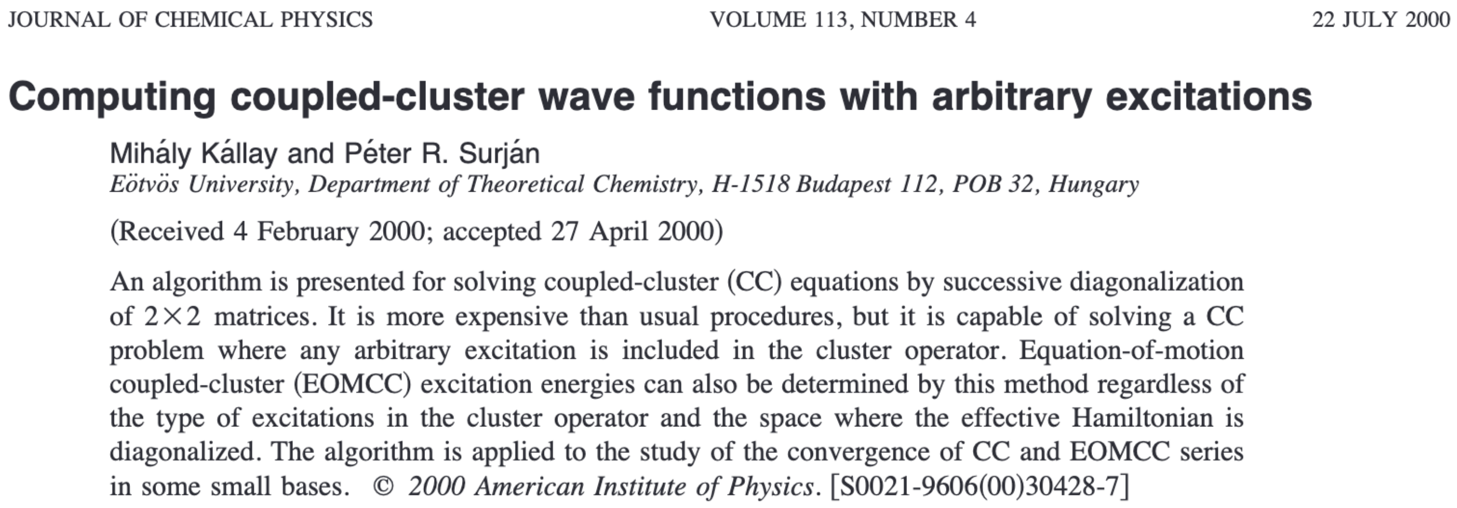
[b] *Chemistry Department, Princeton University, Princeton, NJ 08540, USA*

Received 7 June 2000; received in final form 2 August 2000

This paper implemented CC with $T$ truncated to rank eight excitations

This paper extended the previous one to equation-of-motion CC with $T$ truncated to rank eight excitations

# *2000: Kállay*



JOURNAL OF CHEMICAL PHYSICS VOLUME 113, NUMBER 4 22 JULY 2000

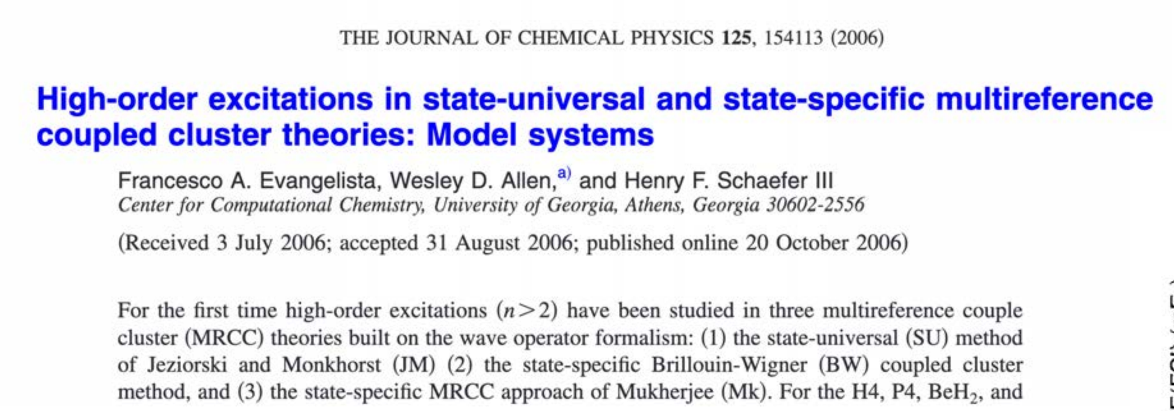
## Computing coupled-cluster wave functions with arbitrary excitations

Mihály Kállay and Péter R. Surján
*Eötvös University, Department of Theoretical Chemistry, H-1518 Budapest 112, POB 32, Hungary*

(Received 4 February 2000; accepted 27 April 2000)

An algorithm is presented for solving coupled-cluster (CC) equations by successive diagonalization of 2×2 matrices. It is more expensive than usual procedures, but it is capable of solving a CC problem where any arbitrary excitation is included in the cluster operator. Equation-of-motion coupled-cluster (EOMCC) excitation energies can also be determined by this method regardless of the type of excitations in the cluster operator and the space where the effective Hamiltonian is diagonalized. The algorithm is applied to the study of the convergence of CC and EOMCC series in some small bases. © *2000 American Institute of Physics*. [S0021-9606(00)30428-7]

# Application to Jeziorski—Monkhorst Multireference CC Methods



THE JOURNAL OF CHEMICAL PHYSICS **125**, 154113 (2006)

**High-order excitations in state-universal and state-specific multireference coupled cluster theories: Model systems**

Francesco A. Evangelista, Wesley D. Allen,[a] and Henry F. Schaefer III
*Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602-2556*

(Received 3 July 2006; accepted 31 August 2006; published online 20 October 2006)

For the first time high-order excitations ($n>2$) have been studied in three multireference couple cluster (MRCC) theories built on the wave operator formalism: (1) the state-universal (SU) method of Jeziorski and Monkhorst (JM) (2) the state-specific Brillouin-Wigner (BW) coupled cluster method, and (3) the state-specific MRCC approach of Mukherjee (Mk). For the H4, P4, $BeH_2$, and

$$|\Psi_{\mathrm{JM}}\rangle = \sum_{\mu}^{d} e^{T^{\mu}} |\Phi_{\mu}\rangle c_{\mu}$$

A linear combination of CC states
(zero internal amplitudes)

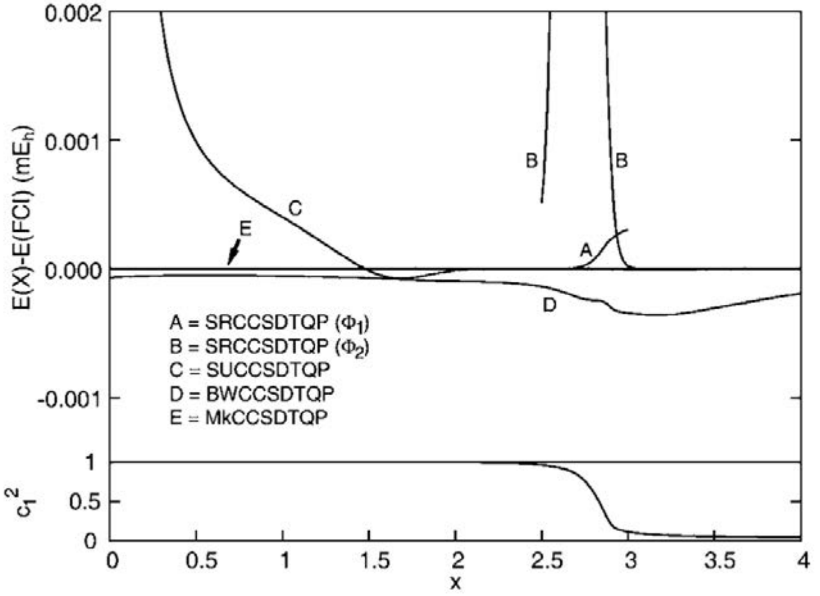
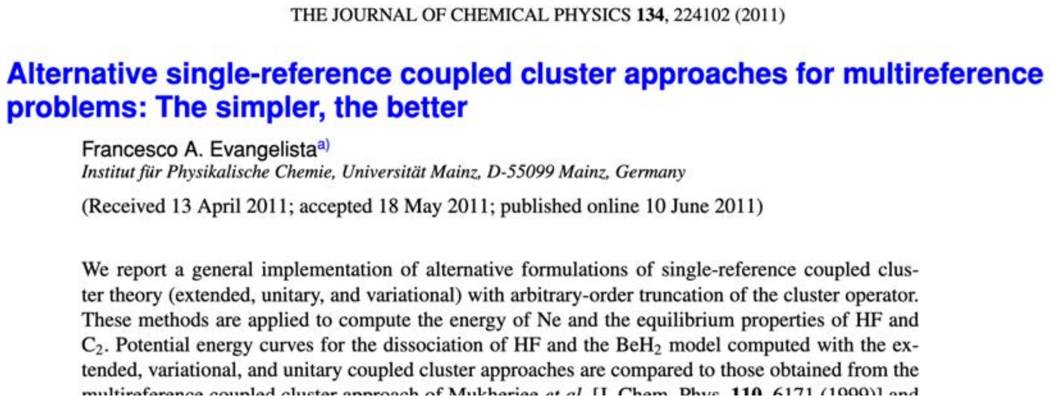


FIG. 12. MRCCSDTQP/[Be(3s2p)/H(2s)] energy curves for the $1\,^1A_1$ ground state of the $BeH_2$ model system. See Fig. 9 caption for details.

# *Application to Alternative CC Methods*



THE JOURNAL OF CHEMICAL PHYSICS **134**, 224102 (2011)

## Alternative single-reference coupled cluster approaches for multireference problems: The simpler, the better

Francesco A. Evangelista[a)]
*Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany*

(Received 13 April 2011; accepted 18 May 2011; published online 10 June 2011)

We report a general implementation of alternative formulations of single-reference coupled cluster theory (extended, unitary, and variational) with arbitrary-order truncation of the cluster operator. These methods are applied to compute the energy of Ne and the equilibrium properties of HF and $C_2$. Potential energy curves for the dissociation of HF and the $BeH_2$ model computed with the extended, variational, and unitary coupled cluster approaches are compared to those obtained from the

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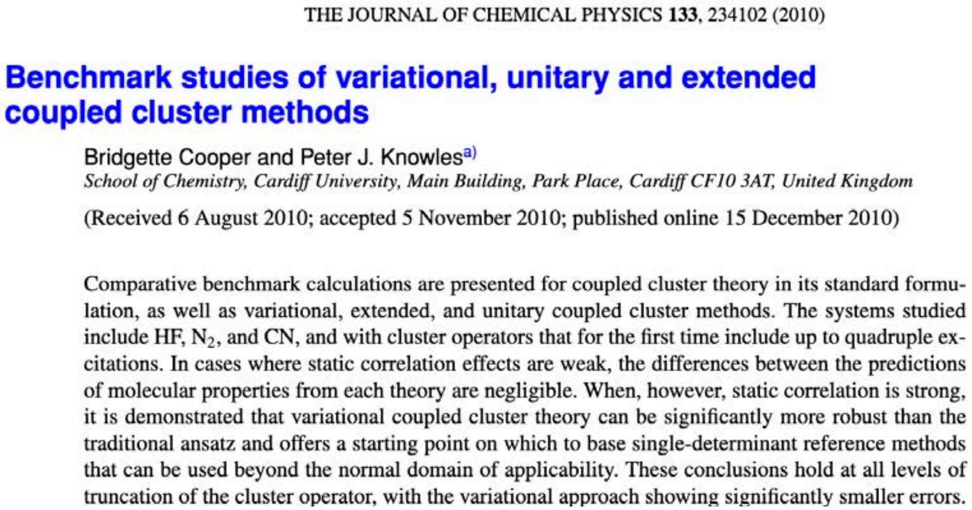

THE JOURNAL OF CHEMICAL PHYSICS **133**, 234102 (2010)

## Benchmark studies of variational, unitary and extended coupled cluster methods

Bridgette Cooper and Peter J. Knowles[a)]
*School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom*

(Received 6 August 2010; accepted 5 November 2010; published online 15 December 2010)

Comparative benchmark calculations are presented for coupled cluster theory in its standard formulation, as well as variational, extended, and unitary coupled cluster methods. The systems studied include HF, $N_2$, and CN, and with cluster operators that for the first time include up to quadruple excitations. In cases where static correlation effects are weak, the differences between the predictions of molecular properties from each theory are negligible. When, however, static correlation is strong, it is demonstrated that variational coupled cluster theory can be significantly more robust than the traditional ansatz and offers a starting point on which to base single-determinant reference methods that can be used beyond the normal domain of applicability. These conclusions hold at all levels of truncation of the cluster operator, with the variational approach showing significantly smaller errors.

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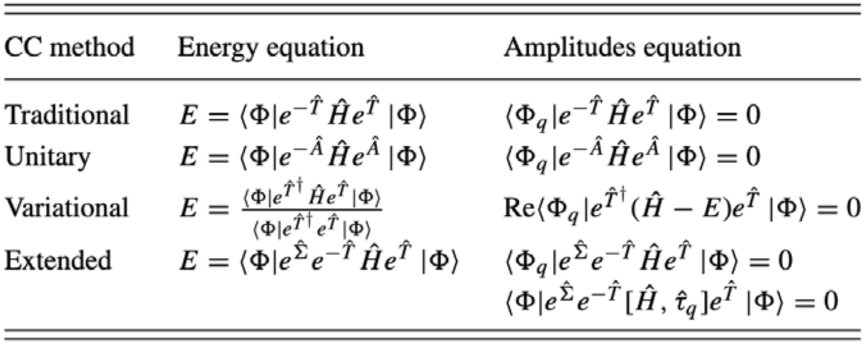
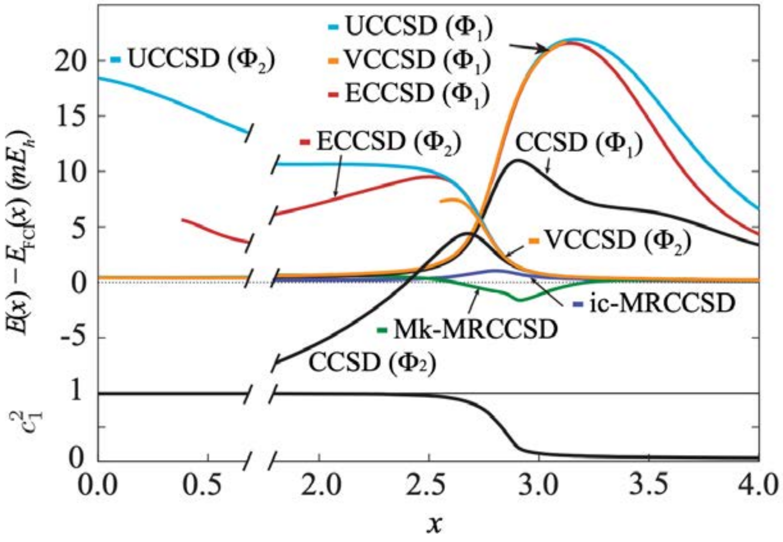
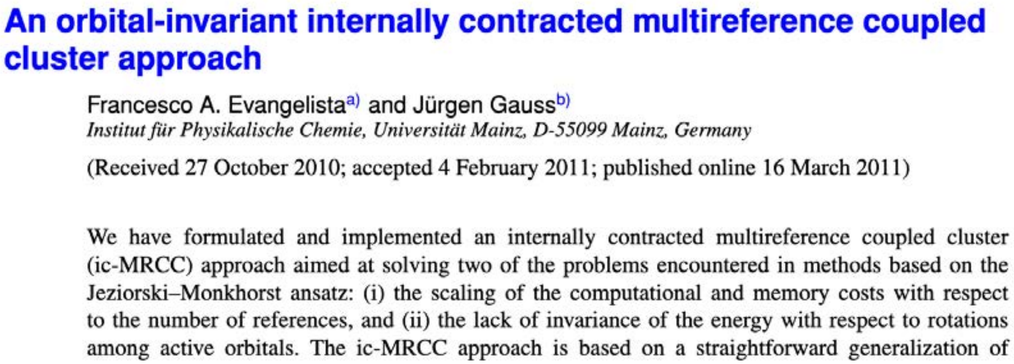


| CC method | Energy equation | Amplitudes equation |
|---|---|---|
| Traditional | $E = \langle\Phi\|e^{-\hat{T}}\hat{H}e^{\hat{T}}\|\Phi\rangle$ | $\langle\Phi_q\|e^{-\hat{T}}\hat{H}e^{\hat{T}}\|\Phi\rangle = 0$ |
| Unitary | $E = \langle\Phi\|e^{-\hat{A}}\hat{H}e^{\hat{A}}\|\Phi\rangle$ | $\langle\Phi_q\|e^{-\hat{A}}\hat{H}e^{\hat{A}}\|\Phi\rangle = 0$ |
| Variational | $E = \frac{\langle\Phi\|e^{\hat{T}^\dagger}\hat{H}e^{\hat{T}}\|\Phi\rangle}{\langle\Phi\|e^{\hat{T}^\dagger}e^{\hat{T}}\|\Phi\rangle}$ | $\mathrm{Re}\langle\Phi_q\|e^{\hat{T}^\dagger}(\hat{H}-E)e^{\hat{T}}\|\Phi\rangle = 0$ |
| Extended | $E = \langle\Phi\|e^{\hat{\Sigma}}e^{-\hat{T}}\hat{H}e^{\hat{T}}\|\Phi\rangle$ | $\langle\Phi_q\|e^{\hat{\Sigma}}e^{-\hat{T}}\hat{H}e^{\hat{T}}\|\Phi\rangle = 0$<br>$\langle\Phi\|e^{\hat{\Sigma}}e^{-\hat{T}}[\hat{H},\hat{\tau}_q]e^{\hat{T}}\|\Phi\rangle = 0$ |



# Pilot Implementation of Internally-Contracted MRCC Theory



**An orbital-invariant internally contracted multireference coupled cluster approach**

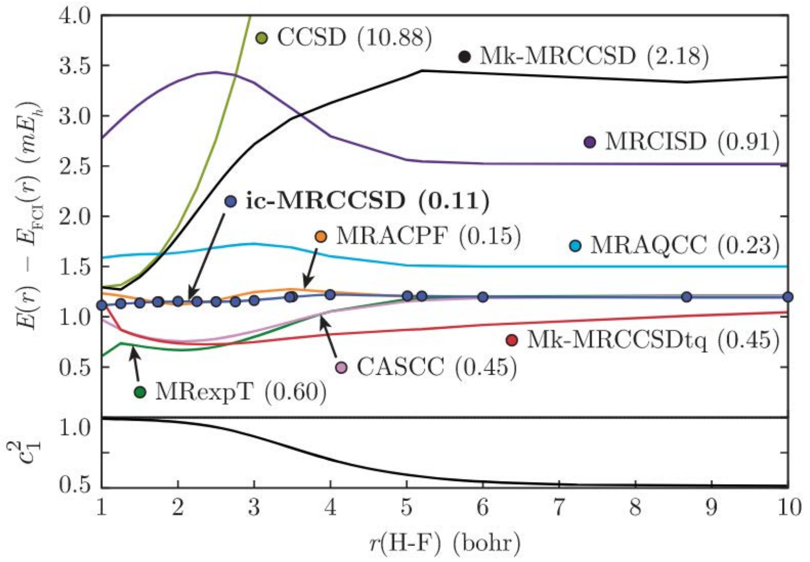
Francesco A. Evangelista[a] and Jürgen Gauss[b]
*Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany*

(Received 27 October 2010; accepted 4 February 2011; published online 16 March 2011)

We have formulated and implemented an internally contracted multireference coupled cluster (ic-MRCC) approach aimed at solving two of the problems encountered in methods based on the Jeziorski–Monkhorst ansatz: (i) the scaling of the computational and memory costs with respect to the number of references, and (ii) the lack of invariance of the energy with respect to rotations among active orbitals. The ic-MRCC approach is based on a straightforward generalization of

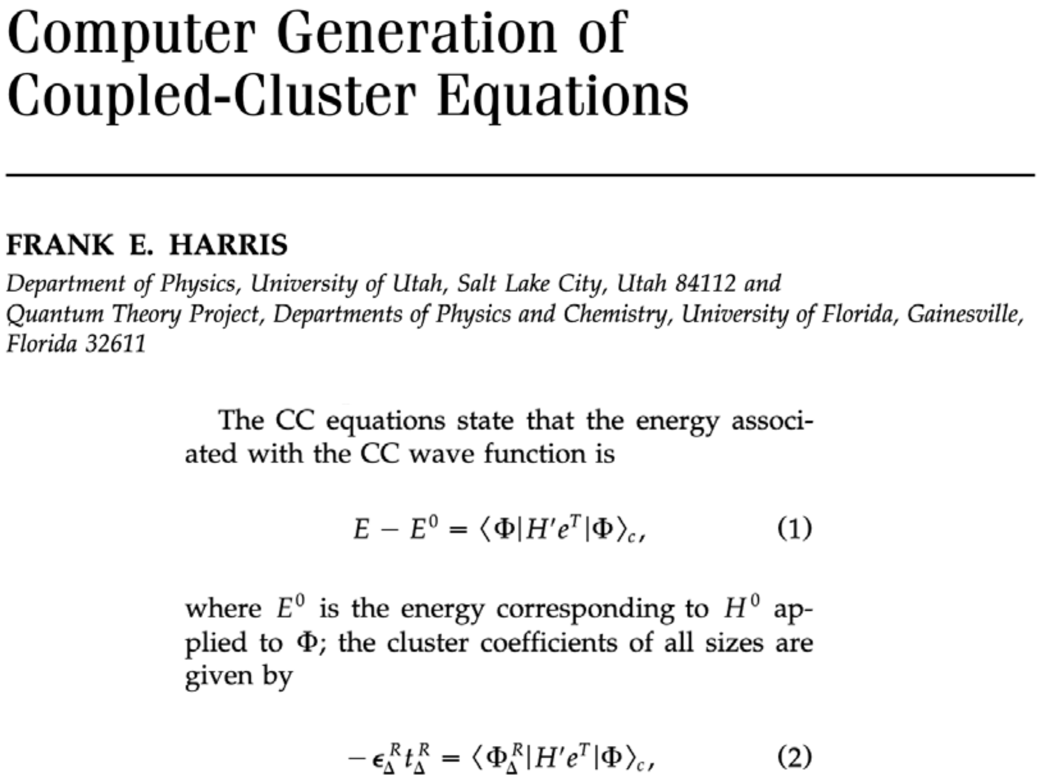
$$|\Psi_{\text{icMRCC}}\rangle = e^{T}\sum_{\mu}^{d}|\Phi_{\mu}\rangle c_{\mu}$$

**One operator applied to a linear combination of determinants**



# *Diagrammatic Approaches*

# *1999: Harris*



## Computer Generation of Coupled-Cluster Equations

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**FRANK E. HARRIS**

*Department of Physics, University of Utah, Salt Lake City, Utah 84112 and Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville, Florida 32611*

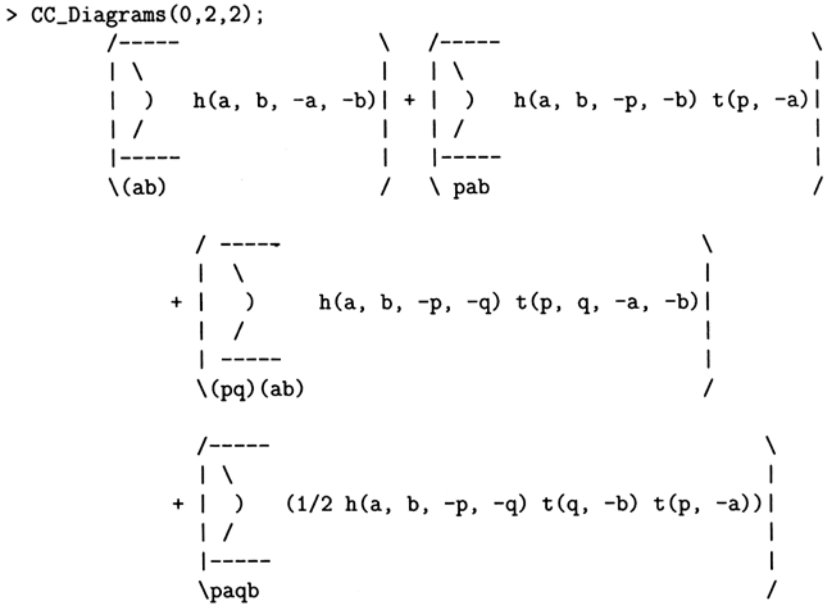
The CC equations state that the energy associated with the CC wave function is

$$E - E^0 = \langle \Phi | H' e^T | \Phi \rangle_c, \qquad (1)$$

where $E^0$ is the energy corresponding to $H^0$ applied to $\Phi$; the cluster coefficients of all sizes are given by

$$-\epsilon_\Delta^R t_\Delta^R = \langle \Phi_\Delta^R | H' e^T | \Phi \rangle_c, \qquad (2)$$

The CC energy diagram



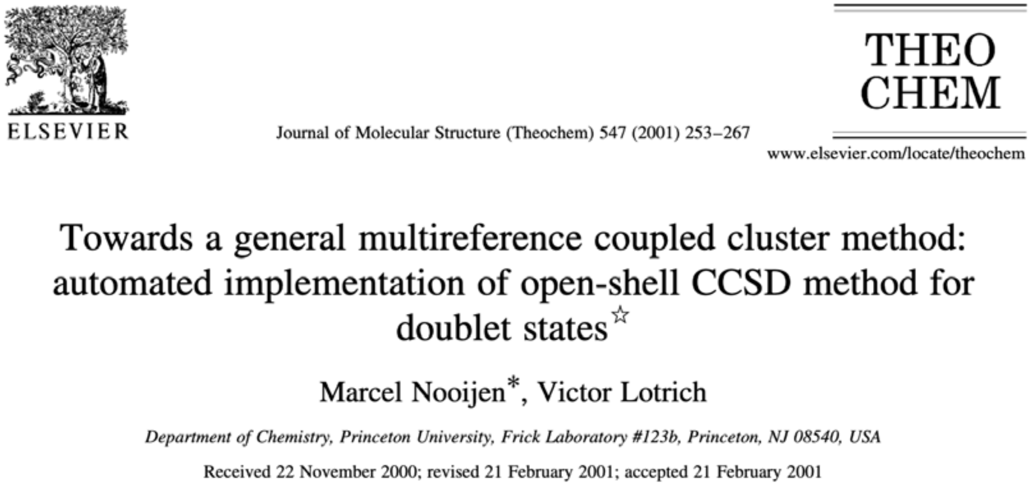
```
> CC_Diagrams(0,2,2);
        /-----                \   /-----                         \
        | \                   |   | \                            |
        |  )   h(a, b, -a, -b)| + |  )   h(a, b, -p, -b) t(p, -a)|
        | /                   |   | /                            |
        |-----                |   |-----                         |
        \(ab)                 /   \ pab                          /

               / -----                                  \
               |  \                                     |
             + |   )     h(a, b, -p, -q) t(p, q, -a, -b)|
               |  /                                     |
               | -----                                  |
               \(pq)(ab)                                /

               /-----                                         \
               | \                                            |
             + |  )    (1/2 h(a, b, -p, -q) t(q, -b) t(p, -a))|
               | /                                            |
               |-----                                         |
               \paqb                                          /
```

F.E. Harris, “Computer generation of coupled-cluster equations,” Int J Quantum Chem **75**(4–5), 593–597 (1999).

# *2001: Nooijen*



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Journal of Molecular Structure (Theochem) 547 (2001) 253–267

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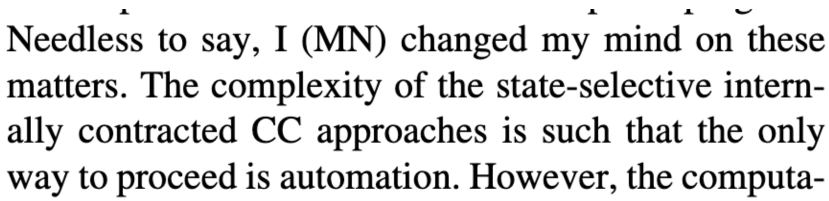
## Towards a general multireference coupled cluster method: automated implementation of open-shell CCSD method for doublet states[☆]

Marcel Nooijen*, Victor Lotrich

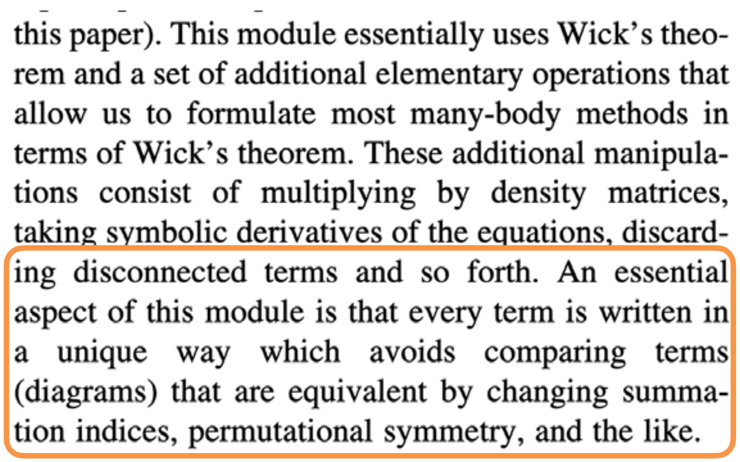
*Department of Chemistry, Princeton University, Frick Laboratory #123b, Princeton, NJ 08540, USA*

Received 22 November 2000; revised 21 February 2001; accepted 21 February 2001



Needless to say, I (MN) changed my mind on these matters. The complexity of the state-selective internally contracted CC approaches is such that the only way to proceed is automation. However, the computa-

Discusses the development of the Automatic Program Generator (APG)



this paper). This module essentially uses Wick's theorem and a set of additional elementary operations that allow us to formulate most many-body methods in terms of Wick's theorem. These additional manipulations consist of multiplying by density matrices, taking symbolic derivatives of the equations, discarding disconnected terms and so forth. An essential aspect of this module is that every term is written in a unique way which avoids comparing terms (diagrams) that are equivalent by changing summation indices, permutational symmetry, and the like.

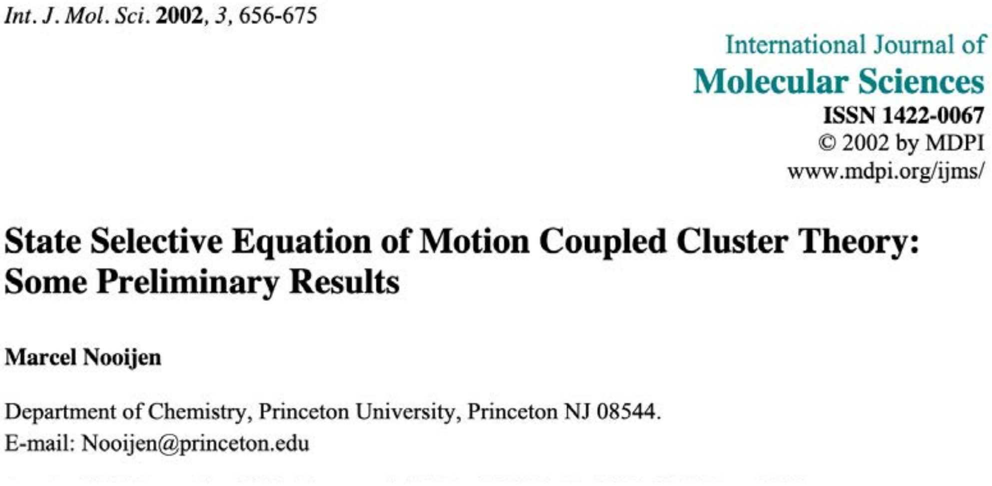
## *2001: Nooijen*

In 2001, Nooijen applied AGP to CC to compute states with +1 or −1 electron with respect to a closed-shell reference $\Phi_c$

$$|\Psi\rangle = e^{T}\{e^{S}\}\ \underbrace{R\,|\Phi_c\rangle}_{\text{open-shell}}$$

E.g., for the ionization case $R = r_m \hat{a}_m$

$S$ is a quasi-particle annihilation operator ($S\,|\Phi_c\rangle = 0$)



*Int. J. Mol. Sci.* **2002**, *3*, 656-675

International Journal of
**Molecular Sciences**
**ISSN 1422-0067**
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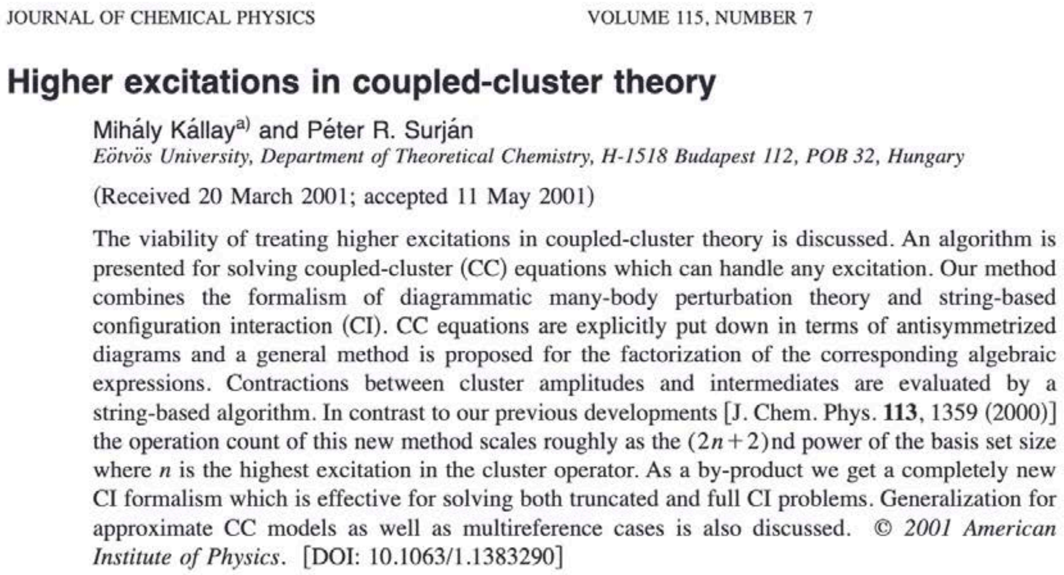
### State Selective Equation of Motion Coupled Cluster Theory: Some Preliminary Results

**Marcel Nooijen**

Department of Chemistry, Princeton University, Princeton NJ 08544.
E-mail: Nooijen@princeton.edu

# 2001: Kállay



JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 7

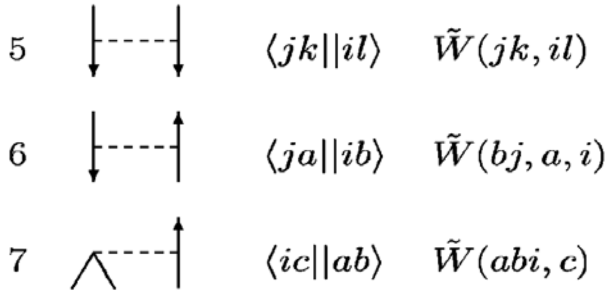
## Higher excitations in coupled-cluster theory

Mihály Kállay[a)] and Péter R. Surján
*Eötvös University, Department of Theoretical Chemistry, H-1518 Budapest 112, POB 32, Hungary*

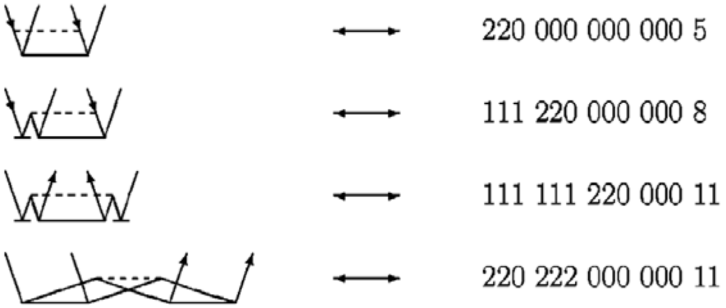
(Received 20 March 2001; accepted 11 May 2001)

The viability of treating higher excitations in coupled-cluster theory is discussed. An algorithm is presented for solving coupled-cluster (CC) equations which can handle any excitation. Our method combines the formalism of diagrammatic many-body perturbation theory and string-based configuration interaction (CI). CC equations are explicitly put down in terms of antisymmetrized diagrams and a general method is proposed for the factorization of the corresponding algebraic expressions. Contractions between cluster amplitudes and intermediates are evaluated by a string-based algorithm. In contrast to our previous developments [J. Chem. Phys. **113**, 1359 (2000)] the operation count of this new method scales roughly as the $(2n+2)$nd power of the basis set size where $n$ is the highest excitation in the cluster operator. As a by-product we get a completely new CI formalism which is effective for solving both truncated and full CI problems. Generalization for approximate CC models as well as multireference cases is also discussed. [DOI: 10.1063/1.1383290]

Interaction vertices are numbered 1–13

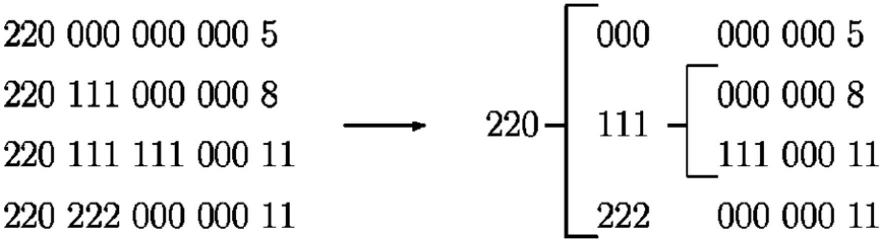


CC diagram represented with simple numerical strings



# *2001: Kállay*

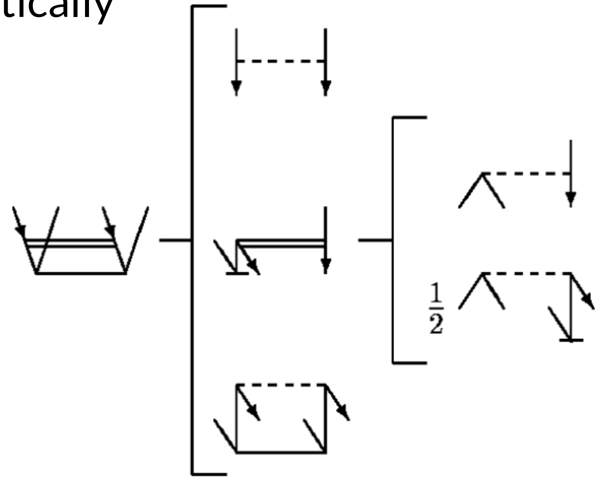
Intermediates can be easily identified

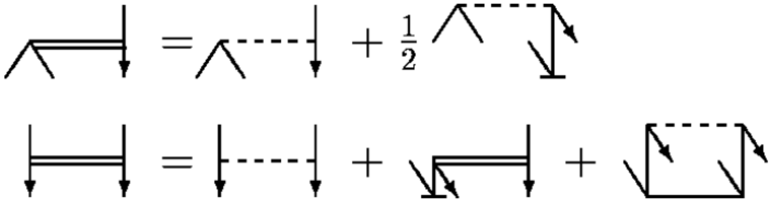


220 000 000 000 5
220 111 000 000 8
220 111 111 000 11
220 222 000 000 11

220
000 000 000 5
111 000 000 8
111 111 000 11
222 000 000 11

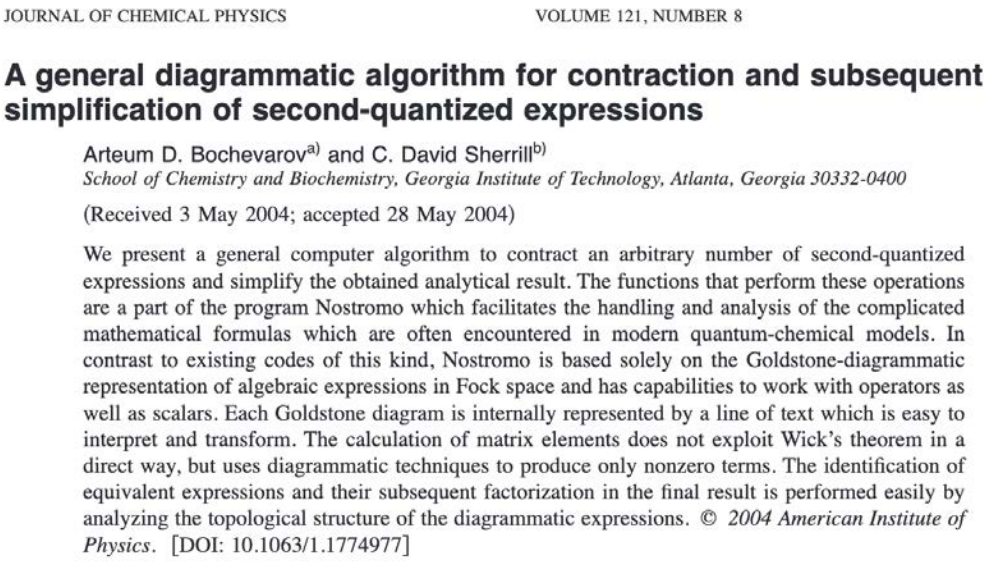
Diagrammatically





**Diagrammatic intermediates**

# 2004: Bochevarov And Sherrill



JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 8

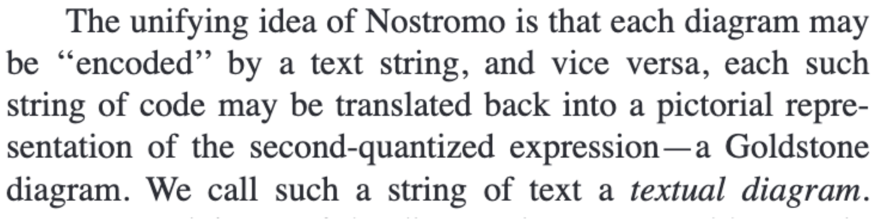
**A general diagrammatic algorithm for contraction and subsequent simplification of second-quantized expressions**

Arteum D. Bochevarov[a] and C. David Sherrill[b]
*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400*

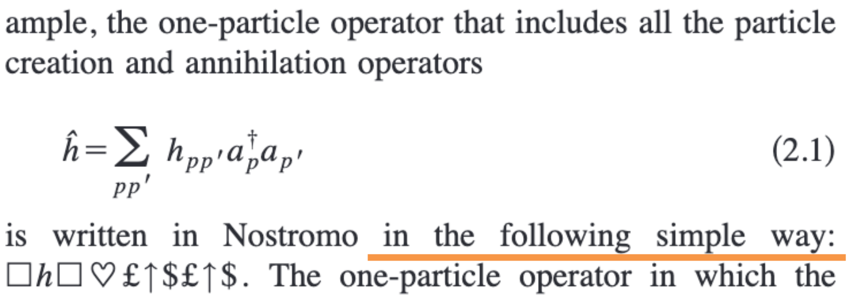
(Received 3 May 2004; accepted 28 May 2004)

We present a general computer algorithm to contract an arbitrary number of second-quantized expressions and simplify the obtained analytical result. The functions that perform these operations are a part of the program Nostromo which facilitates the handling and analysis of the complicated mathematical formulas which are often encountered in modern quantum-chemical models. In contrast to existing codes of this kind, Nostromo is based solely on the Goldstone-diagrammatic representation of algebraic expressions in Fock space and has capabilities to work with operators as well as scalars. Each Goldstone diagram is internally represented by a line of text which is easy to interpret and transform. The calculation of matrix elements does not exploit Wick's theorem in a direct way, but uses diagrammatic techniques to produce only nonzero terms. The identification of equivalent expressions and their subsequent factorization in the final result is performed easily by analyzing the topological structure of the diagrammatic expressions. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1774977]

This independent work developed a Mathematica code called NOSTROMO.



The unifying idea of Nostromo is that each diagram may be "encoded" by a text string, and vice versa, each such string of code may be translated back into a pictorial representation of the second-quantized expression—a Goldstone diagram. We call such a string of text a *textual diagram*.

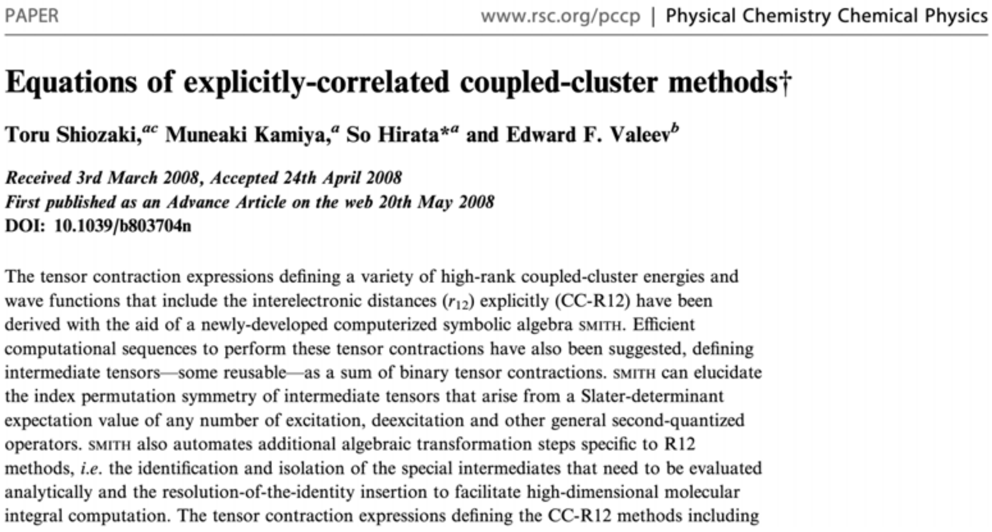


ample, the one-particle operator that includes all the particle creation and annihilation operators

$$\hat{h}=\sum_{pp'} h_{pp'}a_p^\dagger a_{p'} \tag{2.1}$$

is written in Nostromo in the following simple way: □*h*□♡£↑$£↑$. The one-particle operator in which the

# 2008: Shiozaki, Hirata, And Valeev


PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

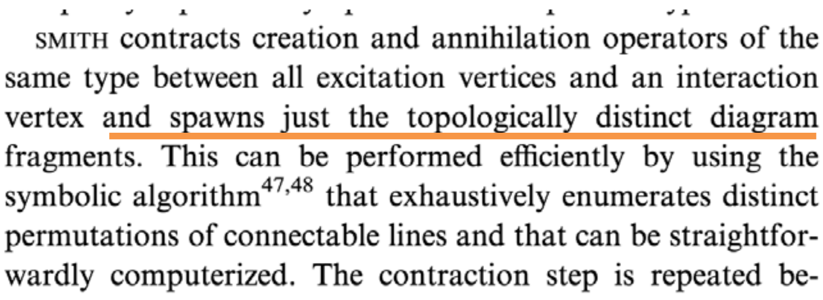
**Equations of explicitly-correlated coupled-cluster methods†**

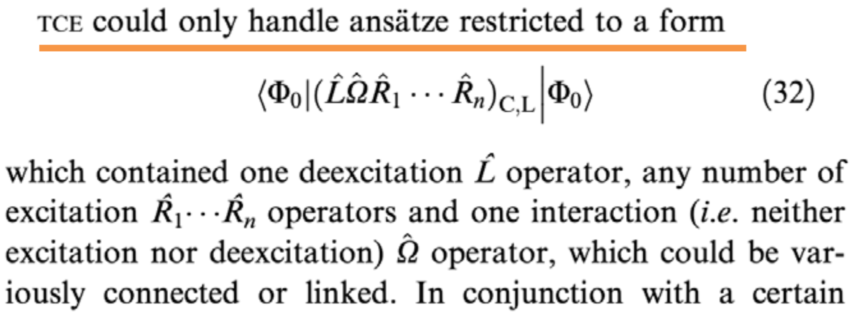
**Toru Shiozaki,[ac] Muneaki Kamiya,[a] So Hirata*[a] and Edward F. Valeev[b]**

*Received 3rd March 2008, Accepted 24th April 2008*
*First published as an Advance Article on the web 20th May 2008*
**DOI: 10.1039/b803704n**

The tensor contraction expressions defining a variety of high-rank coupled-cluster energies and wave functions that include the interelectronic distances ($r_{12}$) explicitly (CC-R12) have been derived with the aid of a newly-developed computerized symbolic algebra SMITH. Efficient computational sequences to perform these tensor contractions have also been suggested, defining intermediate tensors—some reusable—as a sum of binary tensor contractions. SMITH can elucidate the index permutation symmetry of intermediate tensors that arise from a Slater-determinant expectation value of any number of excitation, deexcitation and other general second-quantized operators. SMITH also automates additional algebraic transformation steps specific to R12 methods, *i.e.* the identification and isolation of the special intermediates that need to be evaluated analytically and the resolution-of-the-identity insertion to facilitate high-dimensional molecular integral computation. The tensor contraction expressions defining the CC-R12 methods including

This paper describes SMITH, a successor to the TCE

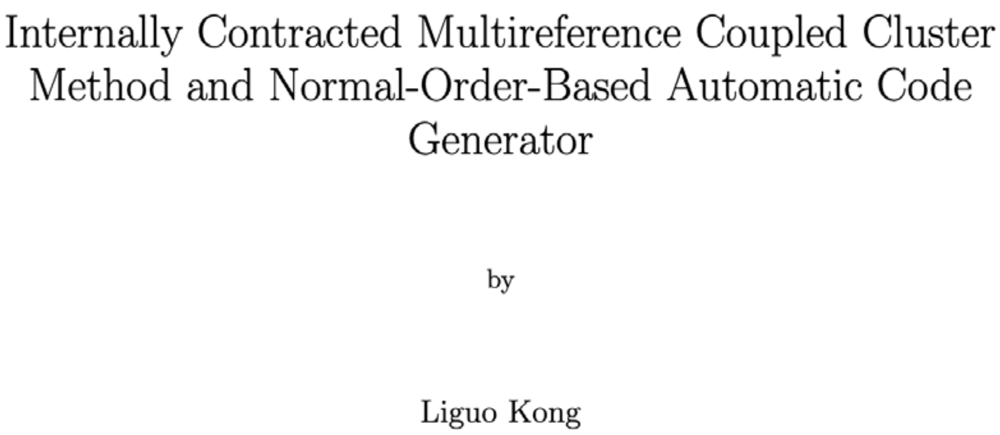

SMITH contracts creation and annihilation operators of the same type between all excitation vertices and an interaction vertex and spawns just the topologically distinct diagram fragments. This can be performed efficiently by using the symbolic algorithm[47,48] that exhaustively enumerates distinct permutations of connectable lines and that can be straightforwardly computerized. The contraction step is repeated be-


TCE could only handle ansätze restricted to a form

$$\langle\Phi_0|(\hat{L}\hat{\Omega}\hat{R}_1\cdots\hat{R}_n)_{\mathrm{C,L}}\Big|\Phi_0\rangle \qquad (32)$$

which contained one deexcitation $\hat{L}$ operator, any number of excitation $\hat{R}_1\cdots\hat{R}_n$ operators and one interaction (*i.e.* neither excitation nor deexcitation) $\hat{\Omega}$ operator, which could be variously connected or linked. In conjunction with a certain

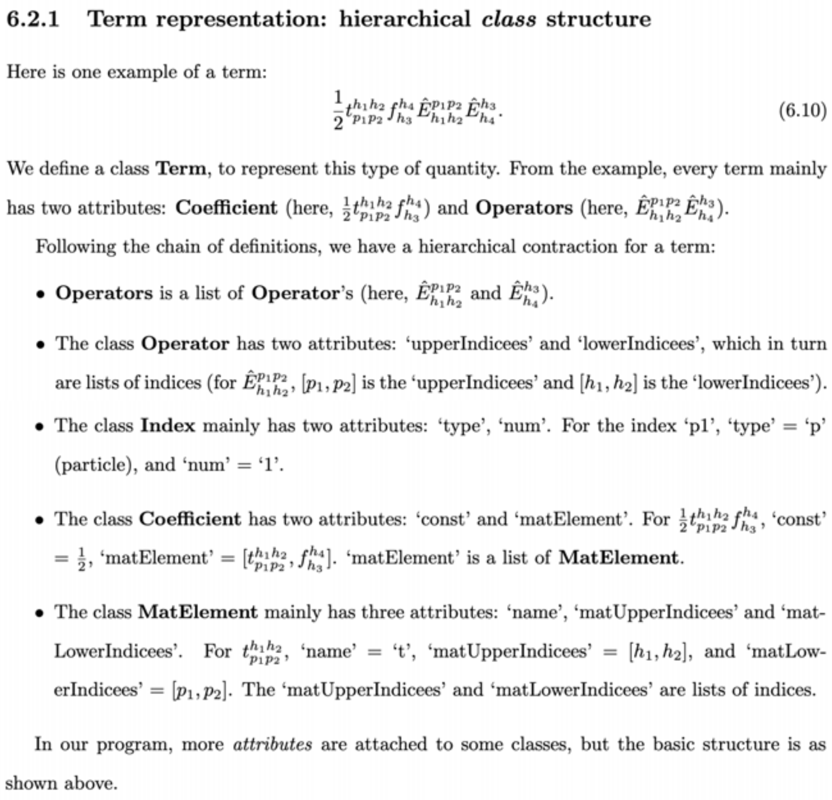
# 2009: Kong Ph.D. Thesis, University of Waterloo (With Nooijen)



Internally Contracted Multireference Coupled Cluster Method and Normal-Order-Based Automatic Code Generator

by

Liguo Kong



### 6.2.1 Term representation: hierarchical *class* structure

Here is one example of a term:

$$\frac{1}{2} t^{h_1 h_2}_{p_1 p_2} f^{h_4}_{h_3} \hat{E}^{p_1 p_2}_{h_1 h_2} \hat{E}^{h_3}_{h_4}. \tag{6.10}$$

We define a class **Term**, to represent this type of quantity. From the example, every term mainly has two attributes: **Coefficient** (here, $\frac{1}{2} t^{h_1 h_2}_{p_1 p_2} f^{h_4}_{h_3}$) and **Operators** (here, $\hat{E}^{p_1 p_2}_{h_1 h_2} \hat{E}^{h_3}_{h_4}$).

Following the chain of definitions, we have a hierarchical contraction for a term:

- **Operators** is a list of **Operator**'s (here, $\hat{E}^{p_1 p_2}_{h_1 h_2}$ and $\hat{E}^{h_3}_{h_4}$).
- The class **Operator** has two attributes: 'upperIndicees' and 'lowerIndicees', which in turn are lists of indices (for $\hat{E}^{p_1 p_2}_{h_1 h_2}$, $[p_1, p_2]$ is the 'upperIndicees' and $[h_1, h_2]$ is the 'lowerIndicees').
- The class **Index** mainly has two attributes: 'type', 'num'. For the index 'p1', 'type' = 'p' (particle), and 'num' = '1'.
- The class **Coefficient** has two attributes: 'const' and 'matElement'. For $\frac{1}{2} t^{h_1 h_2}_{p_1 p_2} f^{h_4}_{h_3}$, 'const' $= \frac{1}{2}$, 'matElement' $= [t^{h_1 h_2}_{p_1 p_2}, f^{h_4}_{h_3}]$. 'matElement' is a list of **MatElement**.
- The class **MatElement** mainly has three attributes: 'name', 'matUpperIndicees' and 'matLowerIndicees'. For $t^{h_1 h_2}_{p_1 p_2}$, 'name' = 't', 'matUpperIndicees' $= [h_1, h_2]$, and 'matLowerIndicees' $= [p_1, p_2]$. The 'matUpperIndicees' and 'matLowerIndicees' are lists of indices.

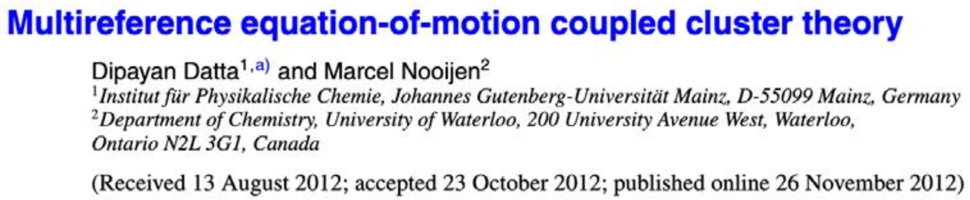
In our program, more *attributes* are attached to some classes, but the basic structure is as shown above.

# 2012: Datta And Nooijen

**A state-specific partially internally contracted multireference coupled cluster approach**

Dipayan Datta,[1,a)] Liguo Kong,[2] and Marcel Nooijen[1]
[1]*Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*
[2]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA*

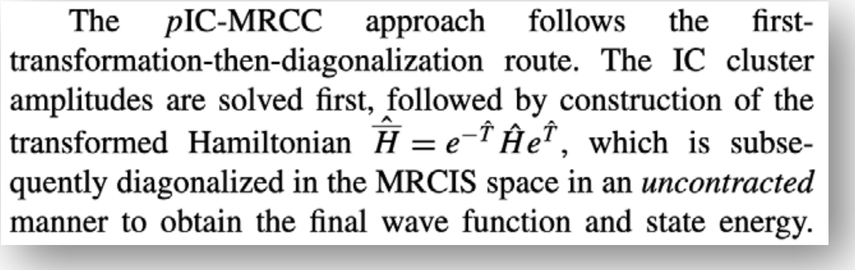
(Received 14 February 2011; accepted 29 April 2011; published online 7 June 2011)



**Multireference equation-of-motion coupled cluster theory**

Dipayan Datta[1,a)] and Marcel Nooijen[2]
[1]*Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, D-55099 Mainz, Germany*
[2]*Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada*

(Received 13 August 2012; accepted 23 October 2012; published online 26 November 2012)



The *p*IC-MRCC approach follows the first-transformation-then-diagonalization route. The IC cluster amplitudes are solved first, followed by construction of the transformed Hamiltonian $\hat{\overline{H}} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$, which is subsequently diagonalized in the MRCIS space in an *uncontracted* manner to obtain the final wave function and state energy.

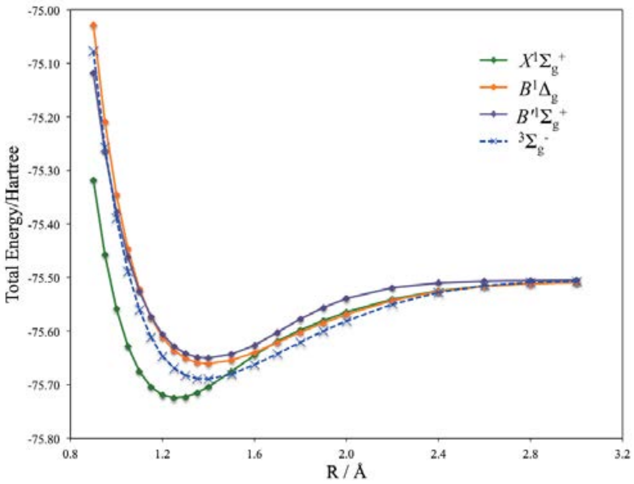
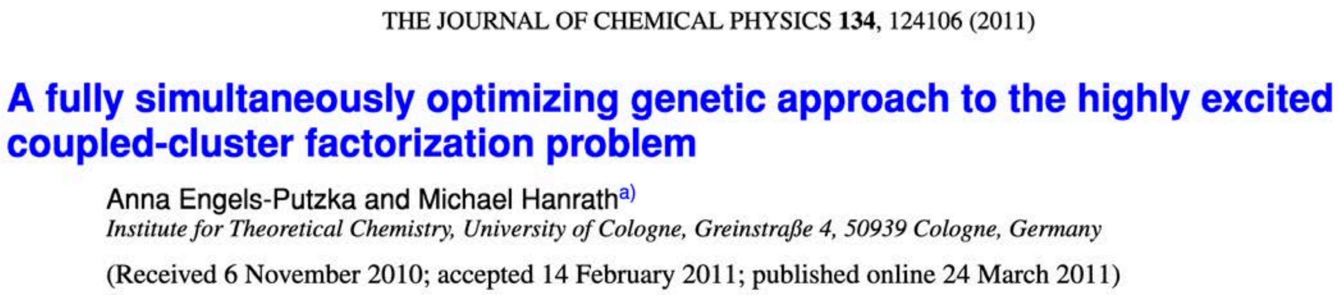


FIG. 1. The potential energy curves for the $X\,^1\Sigma_g^+$, $B^1\Delta_g$, and $B'^1\Sigma_g^+$ states of $C_2$ molecule obtained using the 6-31G* basis and the MR-EOMCC(mb) approach.

Datta, D., Kong, L. & Nooijen, M. *J. Chem. Phys.* **134**, 214116 (2011).
Datta, D. & Nooijen, M. *J. Chem. Phys.* **137**, 204107 (2012).

# 2011: Engels-Putzka and Hanrath

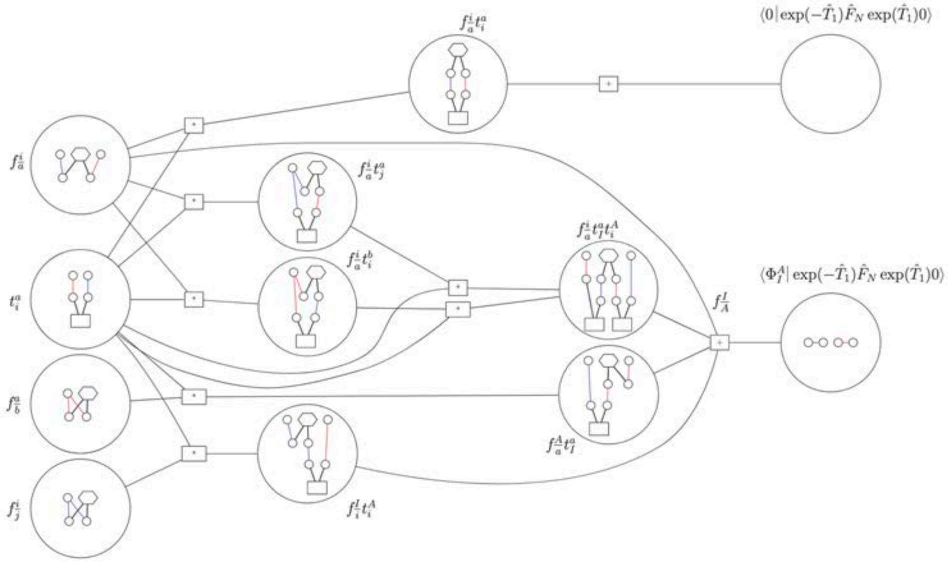


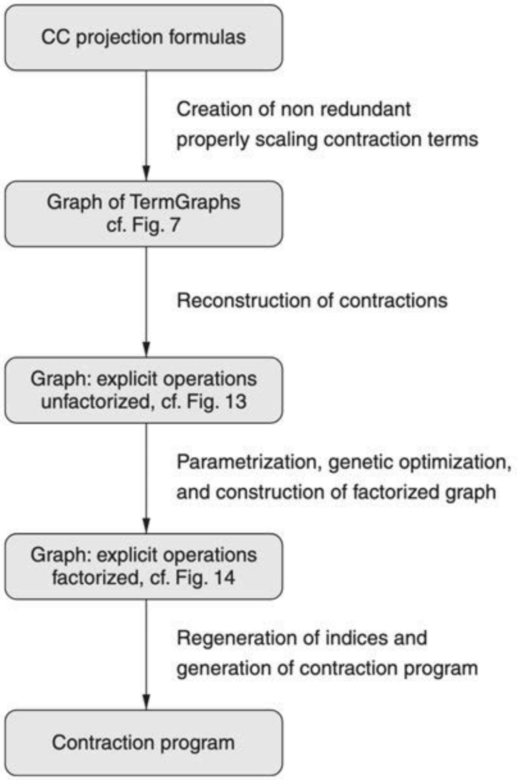
THE JOURNAL OF CHEMICAL PHYSICS **134**, 124106 (2011)

## A fully simultaneously optimizing genetic approach to the highly excited coupled-cluster factorization problem

Anna Engels-Putzka and Michael Hanrath[a)]
*Institute for Theoretical Chemistry, University of Cologne, Greinstraße 4, 50939 Cologne, Germany*

(Received 6 November 2010; accepted 14 February 2011; published online 24 March 2011)





CC projection formulas

Creation of non redundant properly scaling contraction terms

Graph of TermGraphs cf. Fig. 7

Reconstruction of contractions

Graph: explicit operations unfactorized, cf. Fig. 13

Parametrization, genetic optimization, and construction of factorized graph

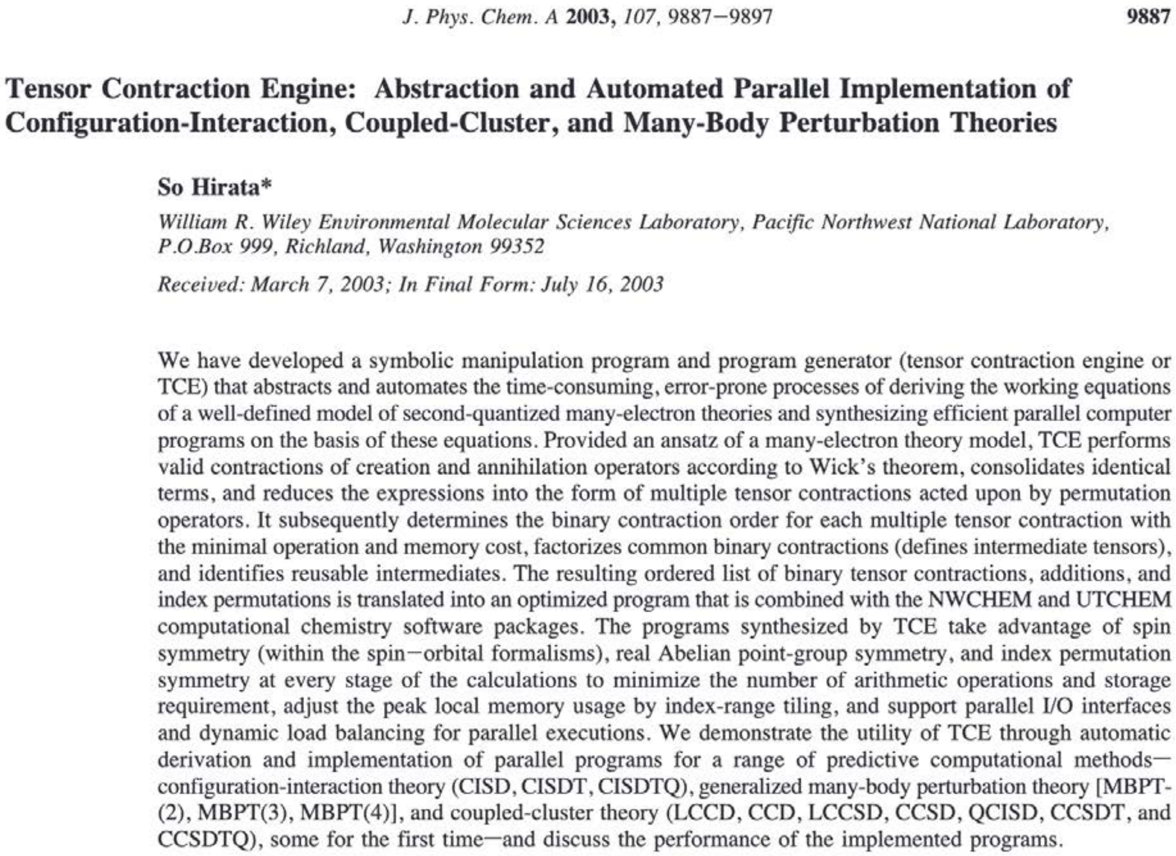
Graph: explicit operations factorized, cf. Fig. 14

Regeneration of indices and generation of contraction program

Contraction program

# *Algebraic Approaches*

# 2003: Hirata (TCE)



J. Phys. Chem. A **2003,** *107,* 9887−9897 **9887**

## Tensor Contraction Engine: Abstraction and Automated Parallel Implementation of Configuration-Interaction, Coupled-Cluster, and Many-Body Perturbation Theories

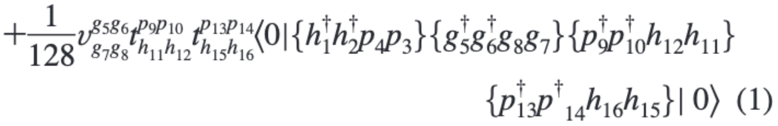
**So Hirata***

*William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O.Box 999, Richland, Washington 99352*

*Received: March 7, 2003; In Final Form: July 16, 2003*

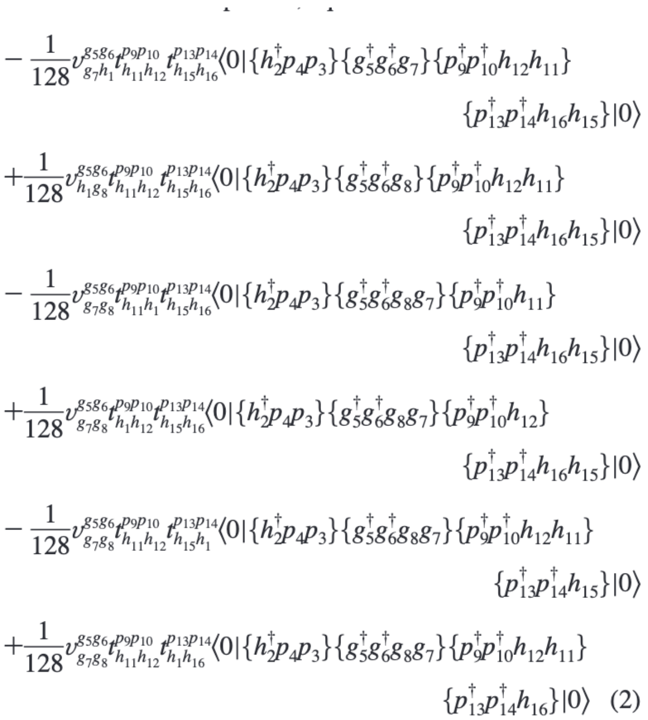
We have developed a symbolic manipulation program and program generator (tensor contraction engine or TCE) that abstracts and automates the time-consuming, error-prone processes of deriving the working equations of a well-defined model of second-quantized many-electron theories and synthesizing efficient parallel computer programs on the basis of these equations. Provided an ansatz of a many-electron theory model, TCE performs valid contractions of creation and annihilation operators according to Wick's theorem, consolidates identical terms, and reduces the expressions into the form of multiple tensor contractions acted upon by permutation operators. It subsequently determines the binary contraction order for each multiple tensor contraction with the minimal operation and memory cost, factorizes common binary contractions (defines intermediate tensors), and identifies reusable intermediates. The resulting ordered list of binary tensor contractions, additions, and index permutations is translated into an optimized program that is combined with the NWCHEM and UTCHEM computational chemistry software packages. The programs synthesized by TCE take advantage of spin symmetry (within the spin−orbital formalisms), real Abelian point-group symmetry, and index permutation symmetry at every stage of the calculations to minimize the number of arithmetic operations and storage requirement, adjust the peak local memory usage by index-range tiling, and support parallel I/O interfaces and dynamic load balancing for parallel executions. We demonstrate the utility of TCE through automatic derivation and implementation of parallel programs for a range of predictive computational methods—configuration-interaction theory (CISD, CISDT, CISDTQ), generalized many-body perturbation theory [MBPT(2), MBPT(3), MBPT(4)], and coupled-cluster theory (LCCD, CCD, LCCSD, CCSD, QCISD, CCSDT, and CCSDTQ), some for the first time—and discuss the performance of the implemented programs.

Hirata, S. *Journal Of Physical Chemistry A* **107**, 9887–9897 (2003).



$$+\frac{1}{128}v^{g_5g_6}_{g_7g_8}t^{p_9p_{10}}_{h_{11}h_{12}}t^{p_{13}p_{14}}_{h_{15}h_{16}}\langle 0|\{h_1^\dagger h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8g_7\}\{p_9^\dagger p_{10}^\dagger h_{12}h_{11}\}\{p_{13}^\dagger p^\dagger{}_{14}h_{16}h_{15}\}|\,0\rangle \quad (1)$$

**Single contraction**



$$-\frac{1}{128}v^{g_5g_6}_{g_7h_1}t^{p_9p_{10}}_{h_{11}h_{12}}t^{p_{13}p_{14}}_{h_{15}h_{16}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_7\}\{p_9^\dagger p_{10}^\dagger h_{12}h_{11}\}\{p_{13}^\dagger p_{14}^\dagger h_{16}h_{15}\}|0\rangle$$

$$+\frac{1}{128}v^{g_5g_6}_{h_1g_8}t^{p_9p_{10}}_{h_{11}h_{12}}t^{p_{13}p_{14}}_{h_{15}h_{16}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8\}\{p_9^\dagger p_{10}^\dagger h_{12}h_{11}\}\{p_{13}^\dagger p_{14}^\dagger h_{16}h_{15}\}|0\rangle$$

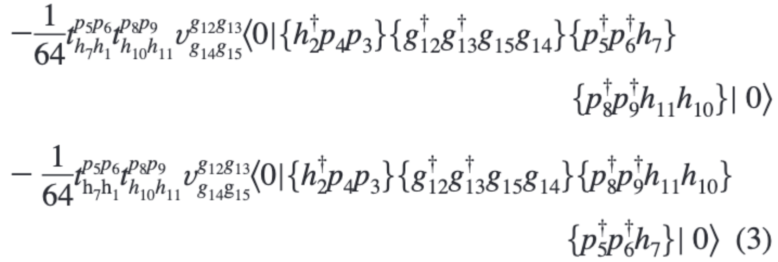
$$-\frac{1}{128}v^{g_5g_6}_{g_7g_8}t^{p_9p_{10}}_{h_{11}h_1}t^{p_{13}p_{14}}_{h_{15}h_{16}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8g_7\}\{p_9^\dagger p_{10}^\dagger h_{11}\}\{p_{13}^\dagger p_{14}^\dagger h_{16}h_{15}\}|0\rangle$$

$$+\frac{1}{128}v^{g_5g_6}_{g_7g_8}t^{p_9p_{10}}_{h_1h_{12}}t^{p_{13}p_{14}}_{h_{15}h_{16}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8g_7\}\{p_9^\dagger p_{10}^\dagger h_{12}\}\{p_{13}^\dagger p_{14}^\dagger h_{16}h_{15}\}|0\rangle$$

$$-\frac{1}{128}v^{g_5g_6}_{g_7g_8}t^{p_9p_{10}}_{h_{11}h_{12}}t^{p_{13}p_{14}}_{h_{15}h_1}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8g_7\}\{p_9^\dagger p_{10}^\dagger h_{12}h_{11}\}\{p_{13}^\dagger p_{14}^\dagger h_{15}\}|0\rangle$$

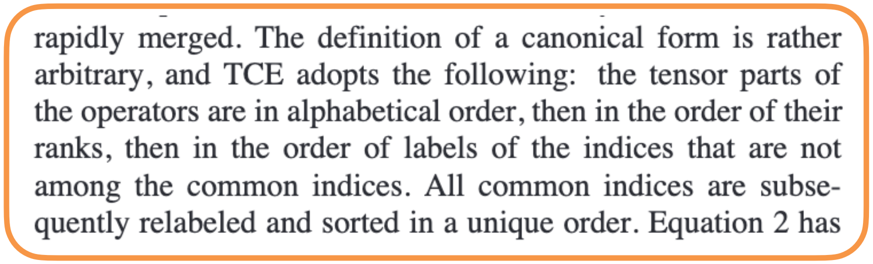
$$+\frac{1}{128}v^{g_5g_6}_{g_7g_8}t^{p_9p_{10}}_{h_{11}h_{12}}t^{p_{13}p_{14}}_{h_1h_{16}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_5^\dagger g_6^\dagger g_8g_7\}\{p_9^\dagger p_{10}^\dagger h_{12}h_{11}\}\{p_{13}^\dagger p_{14}^\dagger h_{16}\}|0\rangle \quad (2)$$

**Canonical form**



$$-\frac{1}{64}t^{p_5p_6}_{h_7h_1}t^{p_8p_9}_{h_{10}h_{11}}v^{g_{12}g_{13}}_{g_{14}g_{15}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_{12}^\dagger g_{13}^\dagger g_{15}g_{14}\}\{p_5^\dagger p_6^\dagger h_7\}\{p_8^\dagger p_9^\dagger h_{11}h_{10}\}|\,0\rangle$$

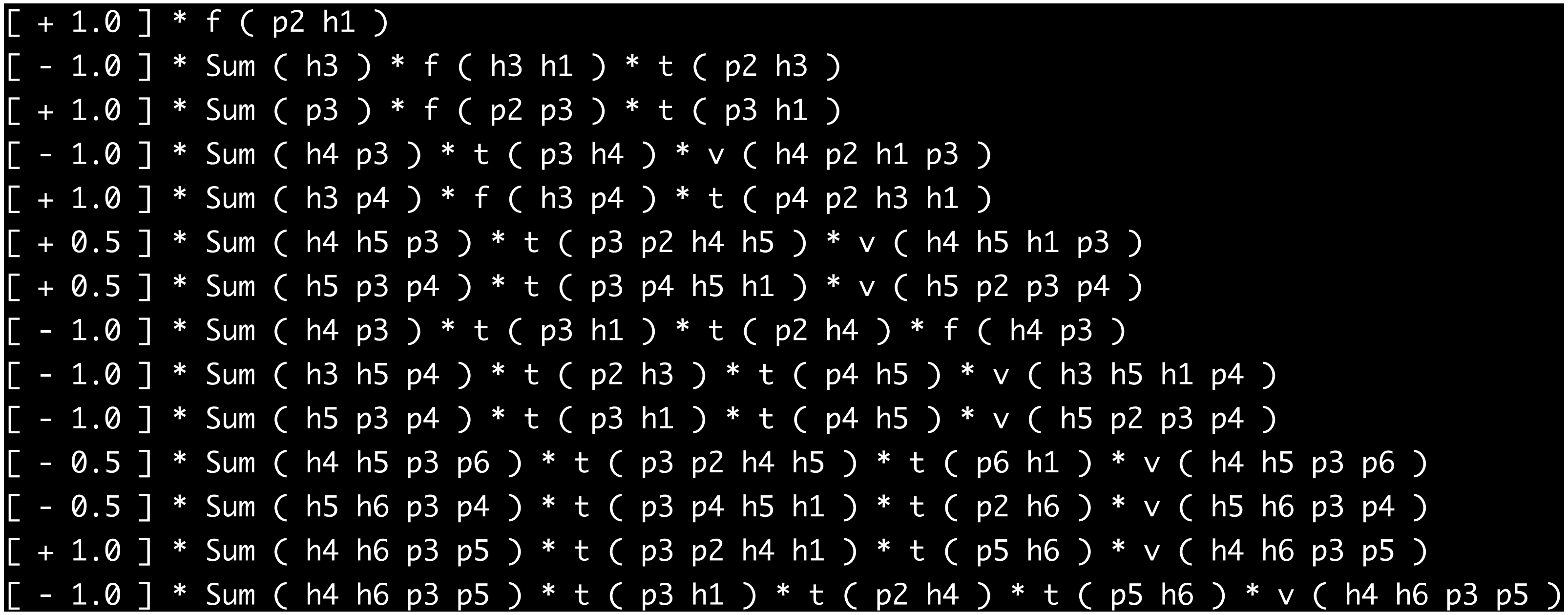
$$-\frac{1}{64}t^{p_5p_6}_{\mathrm{h}_7\mathrm{h}_1}t^{p_8p_9}_{h_{10}h_{11}}v^{g_{12}g_{13}}_{g_{14}\mathrm{g}_{15}}\langle 0|\{h_2^\dagger p_4p_3\}\{g_{12}^\dagger g_{13}^\dagger g_{15}g_{14}\}\{p_8^\dagger p_9^\dagger h_{11}h_{10}\}\{p_5^\dagger p_6^\dagger h_7\}|\,0\rangle \quad (3)$$



rapidly merged. The definition of a canonical form is rather arbitrary, and TCE adopts the following: the tensor parts of the operators are in alphabetical order, then in the order of their ranks, then in the order of labels of the indices that are not among the common indices. All common indices are subsequently relabeled and sorted in a unique order. Equation 2 has

## *Output of the TCE*

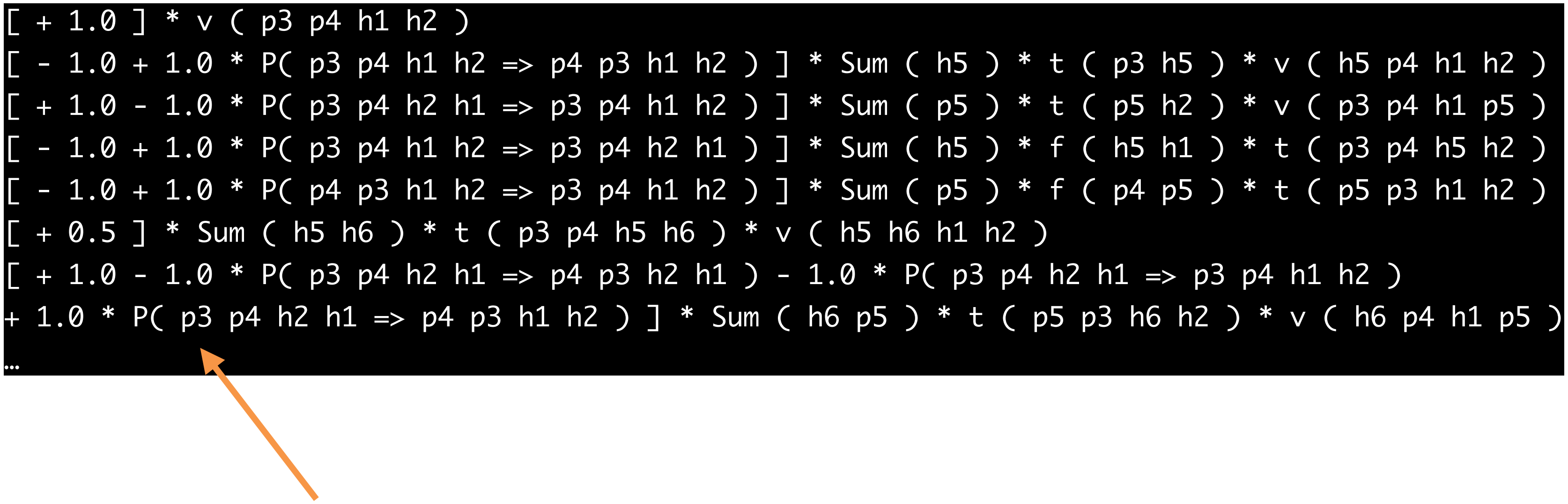
Terms contributing to the CCSD $T_1$ amplitude equation $\langle \Phi_{h_1}^{p_2} | e^{-T} H e^{T} | \Phi \rangle$



```
[ + 1.0 ] * f ( p2 h1 )
[ - 1.0 ] * Sum ( h3 ) * f ( h3 h1 ) * t ( p2 h3 )
[ + 1.0 ] * Sum ( p3 ) * f ( p2 p3 ) * t ( p3 h1 )
[ - 1.0 ] * Sum ( h4 p3 ) * t ( p3 h4 ) * v ( h4 p2 h1 p3 )
[ + 1.0 ] * Sum ( h3 p4 ) * f ( h3 p4 ) * t ( p4 p2 h3 h1 )
[ + 0.5 ] * Sum ( h4 h5 p3 ) * t ( p3 p2 h4 h5 ) * v ( h4 h5 h1 p3 )
[ + 0.5 ] * Sum ( h5 p3 p4 ) * t ( p3 p4 h5 h1 ) * v ( h5 p2 p3 p4 )
[ - 1.0 ] * Sum ( h4 p3 ) * t ( p3 h1 ) * t ( p2 h4 ) * f ( h4 p3 )
[ - 1.0 ] * Sum ( h3 h5 p4 ) * t ( p2 h3 ) * t ( p4 h5 ) * v ( h3 h5 h1 p4 )
[ - 1.0 ] * Sum ( h5 p3 p4 ) * t ( p3 h1 ) * t ( p4 h5 ) * v ( h5 p2 p3 p4 )
[ - 0.5 ] * Sum ( h4 h5 p3 p6 ) * t ( p3 p2 h4 h5 ) * t ( p6 h1 ) * v ( h4 h5 p3 p6 )
[ - 0.5 ] * Sum ( h5 h6 p3 p4 ) * t ( p3 p4 h5 h1 ) * t ( p2 h6 ) * v ( h5 h6 p3 p4 )
[ + 1.0 ] * Sum ( h4 h6 p3 p5 ) * t ( p3 p2 h4 h1 ) * t ( p5 h6 ) * v ( h4 h6 p3 p5 )
[ - 1.0 ] * Sum ( h4 h6 p3 p5 ) * t ( p3 h1 ) * t ( p2 h4 ) * t ( p5 h6 ) * v ( h4 h6 p3 p5 )
```

# *Output of the TCE*

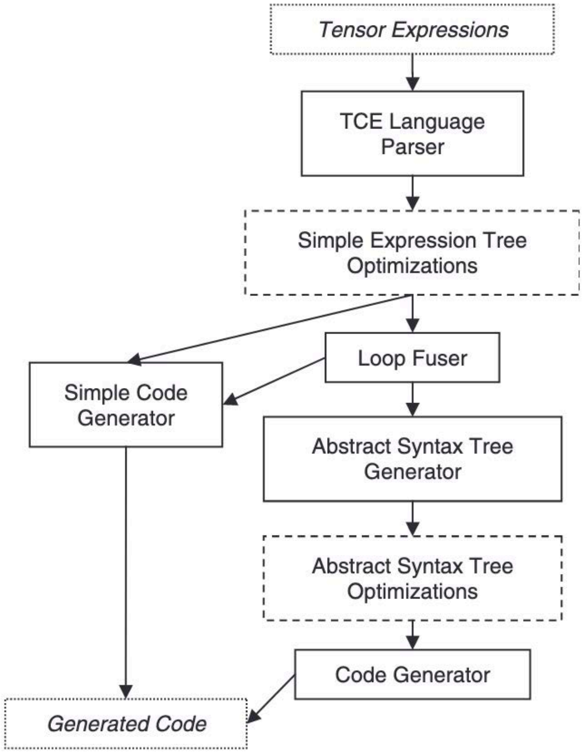
Terms contributing to the CCSD $T_2$ amplitude equation $\langle \Phi_{h_1 h_2}^{p_3 p_4} | e^{-T} H e^{T} | \Phi \rangle$



```
[ + 1.0 ] * v ( p3 p4 h1 h2 )
[ - 1.0 + 1.0 * P( p3 p4 h1 h2 => p4 p3 h1 h2 ) ] * Sum ( h5 ) * t ( p3 h5 ) * v ( h5 p4 h1 h2 )
[ + 1.0 - 1.0 * P( p3 p4 h2 h1 => p3 p4 h1 h2 ) ] * Sum ( p5 ) * t ( p5 h2 ) * v ( p3 p4 h1 p5 )
[ - 1.0 + 1.0 * P( p3 p4 h1 h2 => p3 p4 h2 h1 ) ] * Sum ( h5 ) * f ( h5 h1 ) * t ( p3 p4 h5 h2 )
[ - 1.0 + 1.0 * P( p4 p3 h1 h2 => p3 p4 h1 h2 ) ] * Sum ( p5 ) * f ( p4 p5 ) * t ( p5 p3 h1 h2 )
[ + 0.5 ] * Sum ( h5 h6 ) * t ( p3 p4 h5 h6 ) * v ( h5 h6 h1 h2 )
[ + 1.0 - 1.0 * P( p3 p4 h2 h1 => p4 p3 h2 h1 ) - 1.0 * P( p3 p4 h2 h1 => p3 p4 h1 h2 )
+ 1.0 * P( p3 p4 h2 h1 => p4 p3 h1 h2 ) ] * Sum ( h6 p5 ) * t ( p5 p3 h6 h2 ) * v ( h6 p4 h1 p5 )
…
```

**Permutation operator**

# TCE Optimizations


Tensor Expressions

TCE Language Parser

Simple Expression Tree Optimizations

Loop Fuser

Simple Code Generator

Abstract Syntax Tree Generator

Abstract Syntax Tree Optimizations

Code Generator

Generated Code

The TCE applies several optimizations

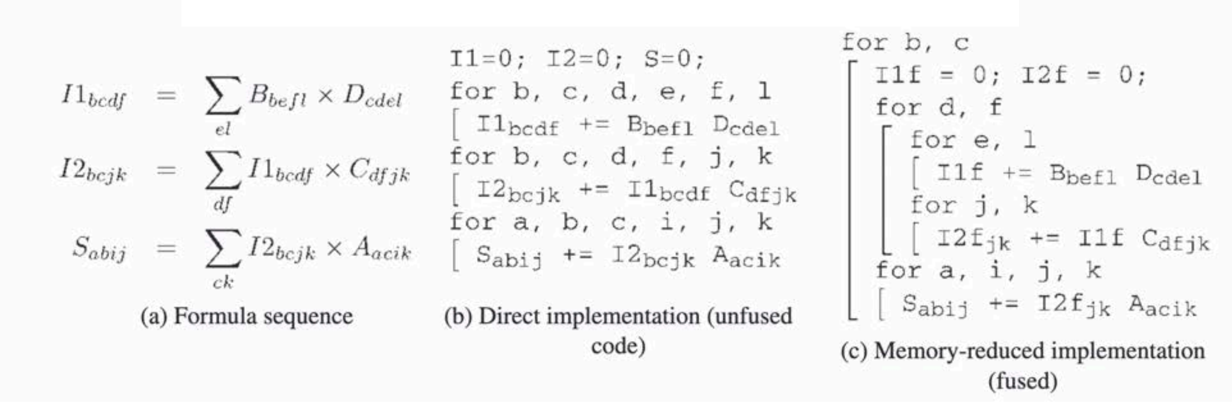
**Expression tree optimization** (introducing intermediates)

**Loop fusion** (minimize memory requirements of intermediates)

**Tiling of arrays** (improve cache performance)

**Parallelism** (run on multiple nodes)

$$S_{abij} = \sum_{cefkl} A_{acik} B_{befl} C_{dfjk} D_{cdel}.$$


$$\begin{aligned} I1_{bcdf} &= \sum_{el} B_{befl} \times D_{cdel} \\ I2_{bcjk} &= \sum_{df} I1_{bcdf} \times C_{dfjk} \\ S_{abij} &= \sum_{ck} I2_{bcjk} \times A_{acik} \end{aligned}$$

(a) Formula sequence

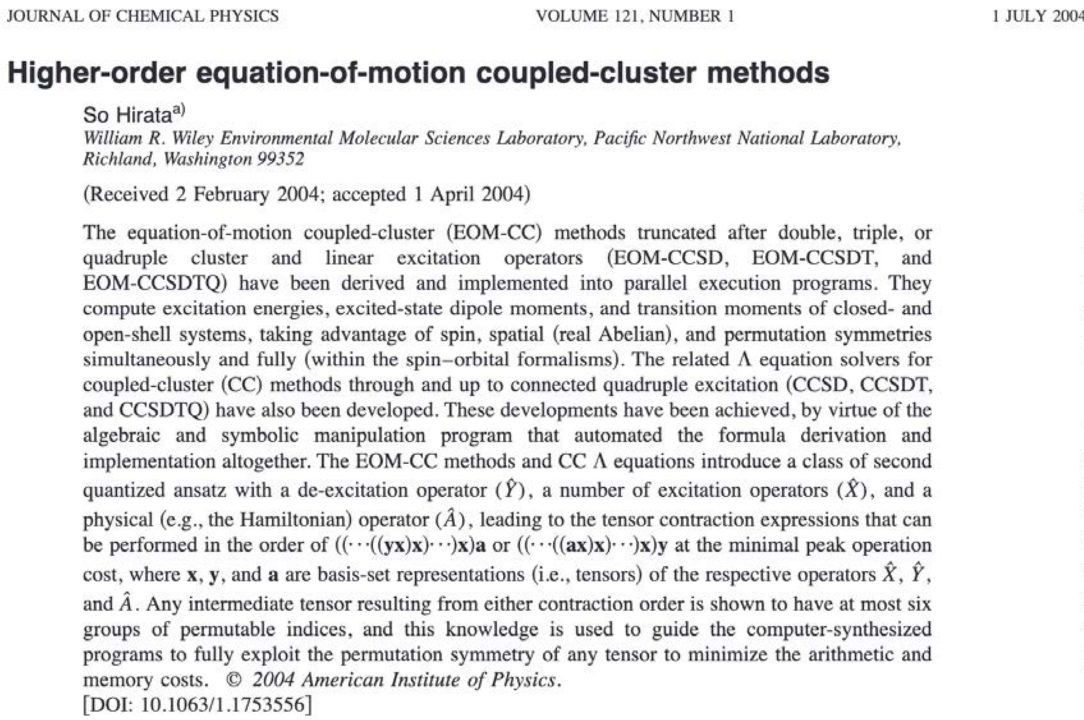
```
I1=0; I2=0; S=0;
for b, c, d, e, f, l
[ I1bcdf += Befl Dcdel
for b, c, d, f, j, k
[ I2bcjk += I1bcdf Cdfjk
for a, b, c, i, j, k
[ Sabij += I2bcjk Aacik
```

(b) Direct implementation (unfused code)

```
for b, c
[ I1f = 0; I2f = 0;
  for d, f
  [ for e, l
    [ I1f += Befl Dcdel
    for j, k
    [ I2fjk += I1f Cdfjk
  for a, i, j, k
  [ Sabij += I2fjk Aacik
```

(c) Memory-reduced implementation (fused)

# *Applications of the TCE*



JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 1 1 JULY 2004

## Higher-order equation-of-motion coupled-cluster methods

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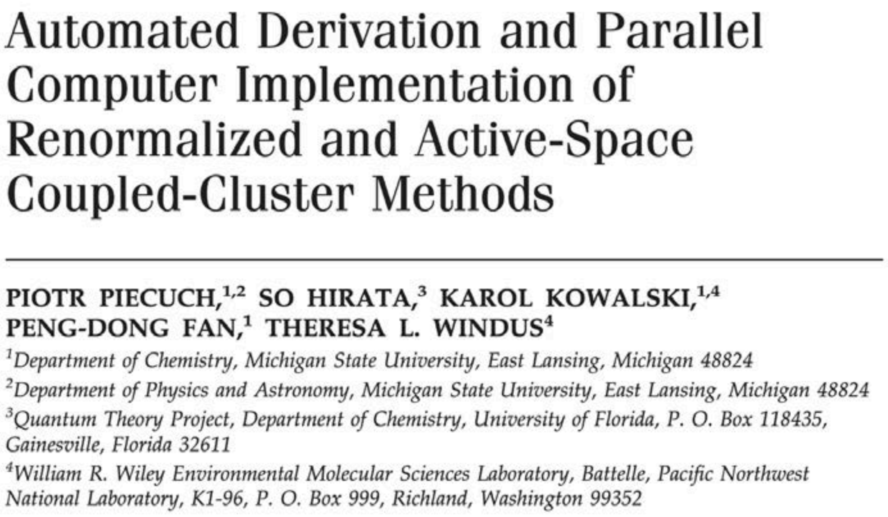
(Received 2 February 2004; accepted 1 April 2004)

The equation-of-motion coupled-cluster (EOM-CC) methods truncated after double, triple, or quadruple cluster and linear excitation operators (EOM-CCSD, EOM-CCSDT, and EOM-CCSDTQ) have been derived and implemented into parallel execution programs. They compute excitation energies, excited-state dipole moments, and transition moments of closed- and open-shell systems, taking advantage of spin, spatial (real Abelian), and permutation symmetries simultaneously and fully (within the spin–orbital formalisms). The related $\Lambda$ equation solvers for coupled-cluster (CC) methods through and up to connected quadruple excitation (CCSD, CCSDT, and CCSDTQ) have also been developed. These developments have been achieved, by virtue of the algebraic and symbolic manipulation program that automated the formula derivation and implementation altogether. The EOM-CC methods and CC $\Lambda$ equations introduce a class of second quantized ansatz with a de-excitation operator $(\hat{Y})$, a number of excitation operators $(\hat{X})$, and a physical (e.g., the Hamiltonian) operator $(\hat{A})$, leading to the tensor contraction expressions that can be performed in the order of $((\cdots((\mathbf{yx})\mathbf{x})\cdots)\mathbf{x})\mathbf{a}$ or $((\cdots((\mathbf{ax})\mathbf{x})\cdots)\mathbf{x})\mathbf{y}$ at the minimal peak operation cost, where $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{a}$ are basis-set representations (i.e., tensors) of the respective operators $\hat{X}$, $\hat{Y}$, and $\hat{A}$. Any intermediate tensor resulting from either contraction order is shown to have at most six groups of permutable indices, and this knowledge is used to guide the computer-synthesized programs to fully exploit the permutation symmetry of any tensor to minimize the arithmetic and memory costs. *© 2004 American Institute of Physics.*
[DOI: 10.1063/1.1753556]



## Automated Derivation and Parallel Computer Implementation of Renormalized and Active-Space Coupled-Cluster Methods

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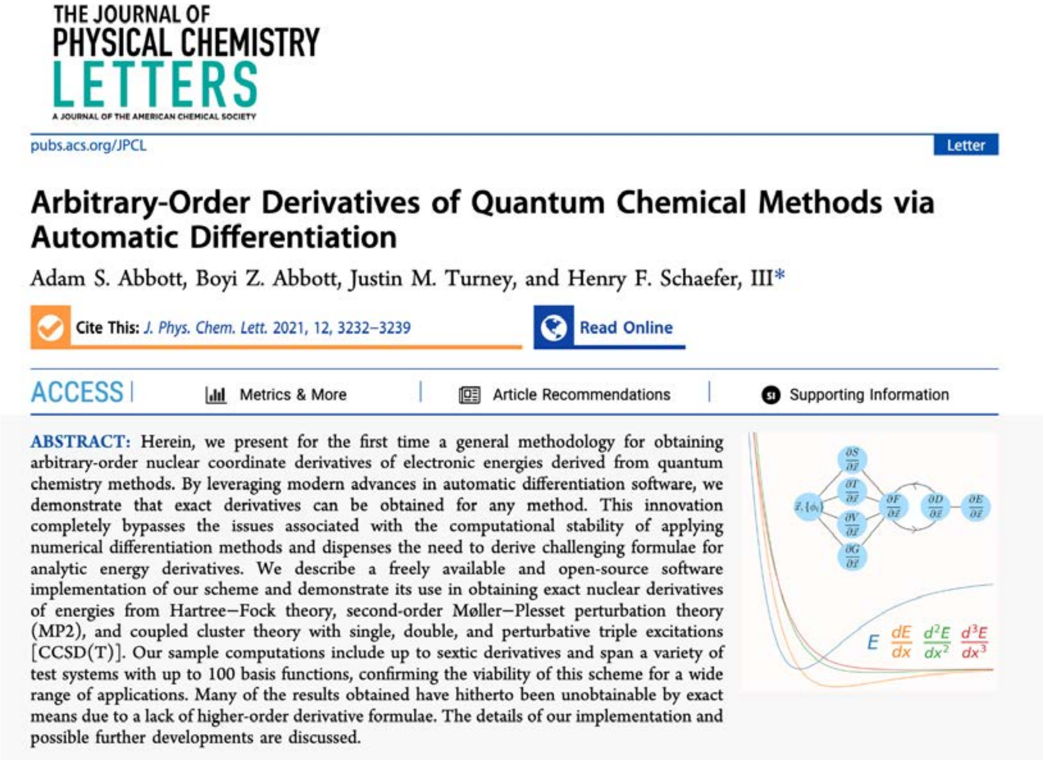
Used the TCE to implement equation-of-motion coupled-cluster methods through CCSDTQ

Used the TCE to implement Piecuch's renormalized CC methods

# *Automation of Energy Derivatives*



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**Arbitrary-Order Derivatives of Quantum Chemical Methods via Automatic Differentiation**

Adam S. Abbott, Boyi Z. Abbott, Justin M. Turney, and Henry F. Schaefer, III*

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 3232−3239

**ABSTRACT:** Herein, we present for the first time a general methodology for obtaining arbitrary-order nuclear coordinate derivatives of electronic energies derived from quantum chemistry methods. By leveraging modern advances in automatic differentiation software, we demonstrate that exact derivatives can be obtained for any method. This innovation completely bypasses the issues associated with the computational stability of applying numerical differentiation methods and dispenses the need to derive challenging formulae for analytic energy derivatives. We describe a freely available and open-source software implementation of our scheme and demonstrate its use in obtaining exact nuclear derivatives of energies from Hartree−Fock theory, second-order Møller−Plesset perturbation theory (MP2), and coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)]. Our sample computations include up to sextic derivatives and span a variety of test systems with up to 100 basis functions, confirming the viability of this scheme for a wide range of applications. Many of the results obtained have hitherto been unobtainable by exact means due to a lack of higher-order derivative formulae. The details of our implementation and possible further developments are discussed.

Here the base theory is coded and the arbitrary-order derivatives with respect to some parameter (geometry, external field) are computed automatically using Google's JAX library.

***The End!***