

From configuration interaction to coupled cluster theory: The quadratic configuration interaction approach

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Configuration interaction (CI) theory has dominated the first 50 years of quantum chemistry before it was replaced by many-body perturbation theory and coupled cluster theory. However, even today it plays an important role in the education of everybody who wants to enter the realm of quantum chemistry. Apart from this, full CI is the method of choice for getting exact energies for a given basis set. The development of CI theory from the early days of quantum chemistry up to our time is described with special emphasis on the size-extensivity problem, which after its discovery has reduced the use of CI methods considerably. It led to the development of the quadratic CI (QCI) approach as a special form of size-extensive CI. Intimately linked with QCI is the scientific dispute between QCI developers and their opponents, who argued that the QCI approach in its original form does not lead to a set of size-extensive CI methods. This dispute was settled when it was shown that QCI in its original form can be converted into a generally defined series of size-extensive methods, which however have to be viewed as a series of simplified coupled cluster methods rather than a series of size-extensive CI methods. © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION AND BASIC TERMS

Configuration interaction (CI) theory was the first *post-HF* (*Hartree–Fock*) [also called *post-SCF* (*self-consistent field*)] method used in the early days of quantum chemistry to correct the mean-field approach (MFA) of HF for a better description of electron–electron interactions. In the early literature, one used the term *superposition of configurations*, which as an acronym would be misleading nowadays because it denotes *spin orbit coupling*. Therefore, we will avoid the latter term in this article.

A number of review articles have focused on CI theory. A state-of-the-art account was given by Shavitt¹ in 1977 in *Methods of Electronic Structure*

Theory edited by Schaefer. In the same book, Roos and Siegbahn² and Meyer³ reported on related developments in CI theory thus complementing Shavitt's review. In 1998, Čársky⁴ summarized in an excellent review developments during 70 years of CI theory and 1 year later Sherill and Schaefer gave a detailed account on highly correlated CI theory.⁵

Since CI theory has played such a fundamental role in the development, understanding, and application of electron correlation methods, it is discussed in literally all textbooks on quantum chemistry of which only the book by Szabo and Ostlund⁶ is mentioned here. In the following, some basic terms will be introduced that facilitate the reading of this review.

HF theory simplifies the description of the interactions of N electrons by considering just one electron interacting with the mean field of the $N - 1$ remaining electrons thus reducing the many-body (many-electron) problem to an effective one-body (one-electron) problem. This is the essence of the

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MFA, which implies a drastic simplification of the description of electron–electron interactions. The HF space orbitals ϕ_i or spin orbitals ψ_i (subscripts i, j, k, l, \dots denote orbitals with occupation numbers $n_i = 2, 1$, or 0 in the case of space orbitals or $n_i = 1$ or 0 in the case of spin orbitals) are calculated variationally as a linear combination of M basis functions χ_μ :

$$\phi_i = \sum_{\mu}^M c_{\mu i} \chi_{\mu} \quad \text{with} \quad \mu = 1, 2, \dots, M \quad (1)$$

where the expansion coefficients $c_{\mu i}$ are variationally optimized. Hence, the HF energy $E(\text{HF})$ based on these orbitals is an upper bound to the exact energy $E(\text{exact})$. The difference between the exact, nonrelativistic Schrödinger energy (obtained for a clamped nuclei situation, i.e., with the Born–Oppenheimer approximation) and the HF limit energy (obtained for a complete basis set) is called *correlation energy*⁷:

$$\Delta E(\text{corr}) = E(\text{exact}) - E(\text{HF, limit}) \quad (2)$$

It accounts for the energy lowering due to a correlated movement of the electrons in a many-electron molecule thus reducing the destabilizing electron interactions and correcting in this way the MFA of HF. Since HF is carried out with a finite set of M basis functions, the correlation energy depends on the size of the basis set. It also depends on how the HF method is improved. This can be done in a methodologically simple way by employing CI theory.¹

A set of occupation numbers ($n_1, n_2, n_3, \dots, n_M$) is called an electron configuration. When using space orbitals and describing a closed shell molecule in its ground state, $m = N/2$ orbitals with the lowest energies are doubly occupied. For example, in the case of a VDZ (valence double-zeta) basis set description of the water molecule ($N = 10, M = 13$), the ground state (GS) configuration is given by the occupation vector (22220000000) because there are five doubly occupied ($n_i = 2$) molecular (space) orbitals (MOs) and eight virtual orbitals with $n_a = 0$ (subscripts i and a denote occupied and virtual orbitals, respectively). The corresponding wavefunction is the HF Slater determinant $|\Phi_0\rangle$ derived from the space orbitals, which are expanded by the functions of the VDZ basis set. It has to be noted that the ket vector $|\ \rangle$ is used to denote the quantum state described by the wavefunction in question.

Although the virtual orbitals of a HF calculation have no direct physical meaning (they are by-products of a HF calculation), they can be used in two different ways: (i) They approximate the Dyson orbitals (constructed from *Feynman–Dyson amplitudes*) and their orbital energies the exact electron affinities. In this way, the virtual HF orbitals gain some physi-

cal meaning from the electron attachment process.⁸ (ii) The nodal properties of the virtual HF orbitals (with increasing orbital energies, the number of nodal surfaces of the virtual orbitals increases) can be exploited to improve the HF description of the electron interaction. For this purpose, excited configurations are generated by moving electrons from occupied to virtual orbitals (denoted by subscripts a, b, c , etc.; for orbitals with unspecified electron occupation subscripts p, q, r, s , etc., are used). In the case of the water molecule, doubly (D) excited configurations are for example: (222201100000), (222202000000), or (222200200000). The virtual orbitals possess additional nodal surfaces, which separate two electrons, and therefore a better description of the correlated movements of the electrons is achieved. Depending on the nodal properties of originally and newly occupied orbital, one speaks of in-out ($ns \rightarrow ks$ with $k > n$, etc.), angular ($\sigma \rightarrow \pi^*$), or left-right ($\sigma \rightarrow \sigma^*$) excitations, which describe *in-out*, *angular*, and *left-right* electron correlation, respectively. The corresponding Slater determinants are written in the short form $|\Phi_{ij}^{ab}\rangle$, which indicates that the occupied orbitals ϕ_i and ϕ_j as well as the virtual orbitals ϕ_a and ϕ_b are involved in the excitation process. In this way, a CID (CI with all D excitations) wavefunction can be generated:

$$|\Psi_{\text{CID}}\rangle = c_0 |\Phi_0\rangle + \sum_{i>j}^{a>b} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (3)$$

where c_0 is the coefficient of the HF reference, which can be one or close to one depending on what normalization is used. The c_{ij}^{ab} are the mixing (= *interaction*) coefficients of the excited configurations. Hence, the CID wavefunction is expressed as a linear combination of the HF Slater determinant and all possible D-excited Slater determinants, which can be generated for a set of 13 MOs and 10 electrons. The CID weighting coefficients c_{ij}^{ab} are determined by a variational approach during which the HF orbitals are kept frozen. The resulting CID energy is lower than the HF energy, however still an upper bound to $E(\text{exact})$. The difference $\Delta E(\text{corr, CID}) = E(\text{CID}) - E(\text{HF})$ is the CID correlation energy, which accounts for electron pair correlation effects of the in-out, angular, and left-right type.

In the following, we will express the CI methodology in terms of spin orbitals ψ_i because this is somewhat simpler than working with space orbitals ϕ_i . In general, the functions of a CI expansion such as Eq. (3) are chosen to be eigenfunctions of the spin operators \hat{S}_z and \hat{S}^2 , which commute with the Hamiltonian operator \hat{H} . For molecules with a degenerate

or quasi-degenerate GS, linear combinations of a few Slater determinants rather than single Slater determinants are eigenfunctions of the spin operators, and therefore these spin-adapted configurations are used, which are called *configuration state functions (CSFs)*. For the purpose of simplifying the notation, we keep the symbol $|\Phi_{ijk\dots}^{abc\dots}\rangle$ to denote a CSF, which in the simplest case is identical to one Slater determinant.

A full CI (FCI) expansion for an N -electron system contains all possible P -excitations ($P = S, D, T, Q, \dots, X$), where $|S\rangle = |\Phi_i^a\rangle$ denotes singly(S)-excited CSFs, $|D\rangle = |\Phi_{ij}^{ab}\rangle$ D-excited CSFs, $|T\rangle = |\Phi_{ijk}^{abc}\rangle$ triply(T)-excited CSFs, $|Q\rangle = |\Phi_{ijkl}^{abcd}\rangle$ quadruply(Q)-excited CSFs, and $|X\rangle$ all X -fold excited CSFs.

$$|\Psi_{FCI}\rangle = |\Phi_0\rangle + \sum_{\text{all } P} c_P |\Phi_P\rangle \quad (4)$$

It is convenient to choose the CSFs $|\Phi_P\rangle$ to be orthonormal so that the metric \mathbf{S} becomes the identity matrix \mathbf{I} , and the FCI eigenvalue problem takes the simple form

$$\mathbf{Hc} = \mathbf{E}\mathbf{S}\mathbf{c} = \mathbf{E}\mathbf{c} \quad (5)$$

where the elements of the hermitian matrix \mathbf{H} are given by

$$H_{PQ} = \langle \Phi_P | \hat{H} | \Phi_Q \rangle \quad (6)$$

and the expansion coefficients c_P are collected in the vector \mathbf{c} . The FCI energy of the GS, $E(\text{FCI})$, is defined for the basis set of size M used to obtain the HF reference function $|\Phi_0\rangle$ as the lowest eigenvalue of the diagonal eigenvalue matrix \mathbf{E} .

The HF energy represents a minimum with regard to the mixing of occupied and virtual spin orbitals. Therefore, S -excited CSFs do not interact with the HF GS wavefunction, which is expressed in the Brillouin theorem⁹:

$$\langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = \langle S | \hat{H} | O \rangle = 0 \quad (7)$$

However, as soon as pair correlation or higher n -electron correlation effects are included into the CI expansion, the HF orbitals are no longer optimal. For example, in-out pair correlation requires more diffuse orbitals. By accounting for some of these orbital improvements, the S excitations make a significant contribution in a CISD (CI with all S and D excitations) or any more sophisticated CI wavefunction. The calculation of the matrix elements H_{PQ} follows the Slater rules.^{10,11} One important consequence of the Slater rules is that CSFs differing by more than two spin orbitals do not interact because the Hamiltonian contains just one- and two-particle operators.

Often the orbitals occupied in the HF reference function are called *internal orbitals*. Those orbitals

that substitute the internal orbitals in the CI expansion are called *external orbitals*, where it is generally assumed that the external orbitals are orthogonal to the internal orbitals. As internal orbitals, one can use HF canonical orbitals, natural orbitals, Brueckner orbitals, localized orbitals, etc. External orbitals can be the virtual orbitals of a HF calculations or any type of improved virtual orbitals.

The number of CSF terms in the FCI wavefunction for a system with N electrons, i.e., the size of the FCI space $d(N, S, M)$, can be calculated using Weyl's formula^{1,12,13}

$$d(N, S, M) = \frac{2S+1}{M+1} \binom{M+1}{N/2-S} \binom{M+1}{N/2+S+1} \quad (8)$$

where S is the total spin of the N electron system, $2S+1$ gives its multiplicity, and the symmetry of the system is not considered. Hence for the GS of water calculated with a VDZ basis set ($M=13$), the dimension of the FCI problem expressed in CSFs is 429,429 and increases to 30,046,752 when a valence triple-zeta basis set ($M=19$) is used. The number of Slater determinants is larger by a factor of 3–4, but symmetry can be exploited to reduce this number. In addition, one can carry out a *frozen core* (only the orbitals of the valence shell are used for the generation of CSFs) and/or a *deleted virtual orbital* calculation (a certain number of high-lying virtual orbitals are excluded from the formation of CSF, i.e., they cannot be occupied by electrons) thus reducing the computational load.

Because of the large computational costs, a FCI calculation can only be carried out for relatively small electronic systems. Accordingly, one has used simpler CI expansions that truncate the number of excitations at a given level thus leading to *truncated CI* expansions of the CID, CISD, CI with all S, D , and T excitations (CISDT), or CI with all S, D, T , and Q excitations (CISDTQ) type. If M basis functions (leading to M orbitals) are used, these methods formally scale with $O(M^6)$ (CID and CISD), $O(M^8)$ (CISDT), and $O(M^{10})$ (CISDTQ) where however for large ratios of M/N the computational costs can be reduced to $O(M^4)$ for CISD and even $O(M^6)$ for CISDTQ.

Truncated CI in the form of CISD was once the method of choice, which had to do with its variational character and the upper bound property of the CI energy. For almost 50 years, CI was the most often used *post-SCF* method. In the mid-1970s, first Møller–Plesset perturbation theory,^{14,15} then coupled cluster theory,^{16,17} and finally density functional theory (DFT)¹⁸ replaced CI theory as a basic tool of

a quantum chemist. The reasons for the decreasing application of CI methods will be discussed in the following.

THE EARLY DAYS OF CI THEORY

The first CI calculation was carried out by Hylleraas¹⁹ in 1928 for the helium atom in its ground state.¹⁹ He investigated what one would call today the radial (in-out) correlation of electrons by exciting one or both of the helium electrons into higher lying *ns* atomic orbitals (AOs) thus generating a CI expansion, which led to a significantly lower energy than obtained by the HF approach. Hylleraas also checked the angular correlation and found it to be less important where he was misled by the fact that he could not readjust the in-out excitations when including the angular excitations. In view of his pioneering work on the helium atom, Hylleraas can be called the *father of the CI theory* (as he may also be called the *father of the R12 methods* in view of his second paper on the helium ground state, in which he explicitly introduced the interelectronic distance r_{12} into the wavefunction²⁰).

Despite the fact that CI dates back to the very beginning of quantum chemistry, the lack of computational power and the stagnancy in many parts of science during World War II delayed developments until the 1950s. In 1950, S. F. Boys published a, by today's standards, relatively small CI study of the ground state of the beryllium atom,²¹ which led to an energy clearly below the *HF limit* (i.e., the HF energy obtained with an infinitely large basis set) and which, in terms of computational cost, was less costly than a numerical HF limit calculation. Boys concluded in his paper that CI is the only feasible method for calculating, analyzing, and predicting the electronic structure of atoms and molecules. In the 1950s, Boys and his students at Cambridge (among them I. Shavitt) pushed forward the algorithms and computational techniques to carry out CI calculations.

In 1952, Taylor and Parr²² published CI calculations on the helium atom with four configurations that accounted for 88% of the correlation energy and underlined the importance of angular electron correlation (excitations from 1s to *np* AOs) thus correcting Hylleraas' original CI description of the He atom.

ADVANTAGES OF NATURAL SPIN ORBITALS

In 1955, Löwdin²³ introduced the natural spin orbitals (NSOs), which helped to analyze and understand the wavefunction of a CI calculation. NSOs

are obtained by diagonalizing the one-electron density matrix of the CI wavefunction. They are orbitals with fractional occupation numbers n_i ($0 \leq n_i \leq 1.0$). Löwdin could prove that by using NSOs the CI expansion of most rapid convergence was obtained, which seemed to be of little value since the NSOs have to be determined first by a CI calculation. However, the essence of this finding was already in the same year demonstrated by Shull and Löwdin.²⁴ These authors recalculated the He atom with a three-orbital basis set including all S- and D-substituted configurations (in total six configurations, which corresponds for the two-electron system of He to a FCI calculation), determined the NSOs, and then repeated the calculation by using instead of AOs the calculated NSOs. In this way, it was shown that the number of configurations could be reduced from six to three.

Bender and Davidson²⁵ introduced in 1966 the iterative natural orbital (INO) method, in which the advantage of using NSOs for CI calculations was exploited without having to calculate first the CI density matrix. They started from approximate NSOs calculated for a less-than-complete initial set of configurations. The analysis of the occupation numbers of these NSOs made it possible to eliminate configurations, which turned out to be unimportant. New configurations were then added, and the procedure repeated for an improved CI calculation. When successive iterations (mostly four or five) did not yield any change in the CI expansion, the INO–CI result was obtained. In this way, these authors could obtain 89% of the correlation energy of LiH by using in the end just 45 configurations, which included only 35 of the original 50 configurations in the initial CI guess. The same authors²⁶ could describe diatomic hydrides of the first row with more than 3000 configurations, recovering about 75 % of the correlation energy, which had been unthinkable before that time.

An alternative approach for exploiting the advantages of NSO was suggested in 1966 by Edminston and Krauss²⁷ in the form of the pseudonatural orbital CI (PNO-CI; later also called pair-natural orbital CI). Shull and Löwdin²⁴ had shown that for a two-electron system such as He the use of NSOs reduces the length of the CI expansion from $p(p + 1)$ configurations to just p . Edminston and Krauss exploited this by describing in a many-electron system two electrons located in the same region of space and experiencing the mean field of all other $N - 2$ electrons by a set of approximate NSOs obtained in a small CI calculation. Then, the actual CI calculation was carried out with the PNOs of all electron pairs. Edminston and Krauss investigated in this way just some three-electron systems (He_2^+ , H_3)²⁷; however,

their ideas could be easily generalized if one was prepared to accept that the external orbitals expressed in terms of PNOs are no longer orthogonal for different pairs and therefore an overlap matrix had to be calculated.

It soon turned out that the additional calculations caused by a PNO–CI are less time consuming than was originally believed. In an N -electron system, there are $N(N - 1)/2$ pairs, which can be singlet or triplet coupled. Each of these pairs is described by a set of PNOs where the PNOs are properly located in space. Accordingly, they are superior to HF virtual orbitals as external orbitals in a CI calculation, which gives a PNO–CI method a significant advantage. Meyer developed the first variational PNO–CI method, which was used for a number of accurate CI calculations of the properties of various first row hydrides.^{28,29}

The PNO–CI approach made an important contribution to the development of more efficient CI methods. However, soon it became clear that the use of NSOs only pays out for relatively small CI expansions whereas it is less useful when one considers millions of configurations. NSOs are used nowadays more indirectly when setting up a basis set for a CI calculation. Almlöf and Taylor^{30,31} performed CISD calculations on atoms, determined the corresponding atomic natural orbitals (ANOs), and used their form to set up generally contracted Gaussian basis sets. The corresponding ANO basis sets facilitate the calculation of the correlation energy in a CI expansion because they improve the convergence to the basis set limit.

BOTTLENECKS OF THE CI CALCULATION

A prerequisite for any CI method is the efficient calculation of the matrix elements H_{PQ} of Eq. (6). First steps in this direction were already made by Nesbet³² (a student of Boys) in 1955 when he showed how the calculation of the matrix elements could be simplified by focusing just on the few spin orbitals differing in the reference and excited determinant. A big step forward in the calculation of a CI expansion and the corresponding CI energy was made when the Boys group in Cambridge, UK, programmed each part of a CI calculation for the EDSAC (Electronic Delay Storage Automatic Calculator) electronic computer and presented in 1956 results for small molecules with more than just two electrons.³³ The programming work of the Boys group triggered the development of quantum chemical program packages such

as POLYATOM,³⁴ IBMOL,³⁵ MOLE,³⁶ and Pople's Gaussian70,³⁷ where the latter stood at the beginning of a development that changed the world of quantum chemistry to what it is today: no more tedious and extremely lengthy hand computations on tiny molecules, but extremely intensive high-performance computing including trillions of calculational steps on large molecules such as steroids, proteins, or man-made polymers.

Important steps in this direction were again made by Nesbet as documented in two publications during the 1960s.^{38,39} In the first, he showed that a monstrous $O(M^8)$ calculational bottleneck inherent to CI and all post-HF calculations could be avoided by a much less costly computational procedure. The bottleneck results from the enormous number of two-electron integrals (approximately $M^4/8$) that have to be calculated for a HF description of an electronic system with M basis functions. The solution of the HF–SCF problem requires the calculation of electron interaction integrals expressed in terms of basis functions χ_μ , whereas post-HF methods need the very same electron interaction integrals expressed in terms of spin orbitals. This implies a transformation according to Eq. (9):

$$\langle ij|kl\rangle = \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} c_{i\mu} c_{j\nu} c_{k\lambda} c_{l\sigma} \langle \mu\nu|\lambda\sigma\rangle \quad (9)$$

which corresponds to an $O(M^8)$ calculational load. Nesbet³⁸ made a first step to reduce this load by carrying out the transformation in two steps, which required an intermediate array for storing the semi-transformed integrals. Later, Nesbet's idea was perfected by Bender⁴⁰ who showed that by carrying out the transformation in four steps the calculational costs are reduced from $O(M^8)$ to $O(M^5)$ thus circumventing one of the bottlenecks of a CI calculation.

The other bottleneck of CI calculations resulted from the diagonalization of the large matrix \mathbf{H} of Eq. (5) where often only the lowest eigenvalue is required to obtain the GS energy of an electronic system. Nesbet³⁹ was the first to realize that this simplifies the diagonalization procedure considerably, and he worked out an algorithm to obtain just that lowest eigenvalue and the associated eigenvector rather than all eigenvalues of a large CI matrix. Shavitt and co-workers⁴¹ generalized the Nesbet method to also calculate higher lying eigenvalues. In 1975, Davidson⁴² published the most general solution to the problem by proposing an algorithm that was based on the Lanczos tridiagonalization scheme,⁴³ combined with features of previous solutions to the problem. The Davidson method (which is still used today) converged much

faster, had moderate storage requirements, worked for nearly degenerate eigenvalues, and could also be applied to higher eigenvalues without calculating all lower eigenvalues.⁴²

DIRECT CI AND GUGA CI

A revolution in CI was the introduction of the direct CI method by Roos in 1972.⁴⁴ When using conventional CI methodology, one constructed first each matrix element H_{PQ} from one- and two-electron integrals each multiplied by coupling coefficients, which reflect the occupation and spin-coupling of the spin orbitals in the interacting CSFs $|\Phi_P\rangle$ and $|\Phi_Q\rangle$.

$$H_{PQ} = \sum_i^M \sum_j^M A_{ij}^{PQ} \langle i|\hat{h}|j\rangle + \sum_i^M \sum_j^M \sum_k^M \sum_l^M B_{ijkl}^{PQ} \langle ij|kl\rangle \quad (10)$$

The matrix elements were derived by hand and individually coded into a computer program. In this way, an expansion of just 10,000 configurations led to a total of 5×10^7 matrix elements, which required still millions of H_{PQ} values if just 10% of them was nonzero. These had to be stored on external storage devices before they were read back to solve the CI eigenvalue problem. Roos⁴⁴ avoided the tedious construction of elements H_{PQ} and their storing by directly working with the one- and two-electron integrals

$$\sigma_P = \sum_Q^M \sum_i^M \sum_j^M A_{ij}^{PQ} \langle i|\hat{h}|j\rangle c_Q + \sum_Q^M \sum_i^M \sum_j^M \sum_k^M \sum_l^M B_{ijkl}^{PQ} \langle ij|kl\rangle c_Q \quad (11)$$

which leads to

$$\sigma_P = \mathbf{Hc}_P = E_P \mathbf{c}_P \quad (12)$$

Accordingly, the major task of the direct CI calculation (*direct* because the eigenvalues and eigenvectors are calculated directly from the molecular integrals) is to determine the coupling coefficients A_{ij}^{PQ} and B_{ijkl}^{PQ} . This problem could be facilitated by using the *graphical unitary group approach* (GUGA) or, alternatively, perturbation theory.¹

GUGA is based on the unitary group approach (UGA), which has its roots in nuclear physics. Already in 1950, Gel'fand and Tsetlin^{45,46} had demonstrated how the unitary group $U(M)$ (set of all M -dimensional unitary matrices, for which multiplication, unity ele-

ment, and inverse are defined) can be used to construct an orthonormal basis and to evaluate the matrix elements of the generators of this basis. The importance of this discovery was recognized for the nuclear and the many-electron problem by Moshinsky⁴⁷ and discussed by various authors as for example Matsen and Pauncz.⁴⁸ In 1974, it was Paldus^{13,49} who achieved a considerable simplification of UGA in connection with its application to CI (and perturbation theory) calculations of many-electron systems. He demonstrated that the calculation of the Hamiltonian matrix elements of a CI expansion could be carried out with the help of matrix representatives of the generators \hat{E}_{PQ} of the Gel'fand–Tsetlin formulas.^{13,50} In this approach, individual CSFs were represented by a *Paldus tableaux*.

The significance of Paldus' work on UGA was not directly recognized by the CI community, and therefore it needed a more transparent approach to make UGA attractive as a powerful tool for generating the huge number of matrix elements in the CI calculation of nontrivial molecules. In 1977, Shavitt⁵¹ developed a compact digital representation of excited state configurations in terms of Gel'fand states, which he called the *distinct row table* (DRT).^{51–53} In addition, Shavitt introduced a graphical complement of UGA (GUGA). With the help of GUGA and the *Shavitt graphs* as they are called today, it was possible to represent the DRT in a pictorial way thus yielding a detailed insight into the structure of the CI Hamiltonian matrix.

Brooks and Schaefer⁵⁴ soon presented the first implementation of the GUGA–CI method, which already included the possibility for multireference CI (MR-CI) calculations. When discussing the possibility of GUGA–CI, the authors pointed out that even with a minicomputer CI expansions with 25,000 configurations would soon become accessible. In a second paper, 1 year later, Brooks and co-workers⁵⁵ replaced the previously preferred *integral-driven* approach (i.e., for each molecular integral all productive loops of a Shavitt graph are constructed and all upper and lower *walks* (configurations) are determined; the next integral on the integral list is processed in the same way) by a *loop-driven* algorithm, in which that loop, which can be generated in the easiest way from the previous one, is executed first. The generation of closely related groups of loops and the corresponding blocks of integrals needed for the execution of these loops led to significant time savings.

By connecting Shavitt's GUGA–CI and Roos' direct CI, the coupling coefficients of the later method could be effectively evaluated and used for the calculation of the vector σ_P needed for determination of the

corresponding eigenvalue and eigenvector. In two important publications, Siegbahn^{56,57} showed that the coupling coefficients involving external orbitals adopt a simple structure so that all coupling coefficients can be expressed in terms of equations that involve the relatively small internal space.⁵⁸

FACILITATING THE SOLUTION OF THE CI PROBLEM WITH THE HELP OF PERTURBATION THEORY

The direct CI method can be further improved by using perturbation theory. Already at an early stage of the CI development, perturbation theory was used for a prescreening of individual CSFs and their selection according to their weight in the CI expansion or their contribution to the energy. This can be done in a preliminary calculation by using first-order Rayleigh–Schrödinger perturbation theory according to¹

$$c_P = \frac{\langle \Phi_P | \hat{H} | \Phi_0 \rangle}{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle - \langle \Phi_P | \hat{H} | \Phi_P \rangle} \quad (13)$$

or for the energy contribution

$$\Delta E_P = \frac{|\langle \Phi_P | \hat{H} | \Phi_0 \rangle|^2}{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle - \langle \Phi_P | \hat{H} | \Phi_P \rangle} \quad (14)$$

If one or both parameters are below a preset threshold, the corresponding CSF is eliminated. More sophisticated ways of preselecting the CSFs of a CI expansion have been described in various review articles.^{1,4}

Perturbation theory⁵⁹ can also be used for the calculation of the coefficients of the CI expansion (for convergence problems in the perturbation series, see Ref 15):

$$c_P^{(p)} = (E_P^0 - E_0^0)^{-1} \left[\sum_{r=0}^{p-1} E^{(p-r)} c_P^{(p-r)} - \sum_Q H_{PQ} c_Q^{(p-1)} + c_P^{(p-1)} E_P^0 \right] \quad (15)$$

where

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (16)$$

$$E_0^0 = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle \quad (17)$$

$$E_P^0 = \langle \Phi_P | \hat{H}_0 | \Phi_0 \rangle \quad (18)$$

and

$$\sigma_P^{(p)} = \sum_Q H_{PQ} c_Q^{(p-1)} \quad (19)$$

In this way, the coefficients of the CI expansion are calculated iteratively with the help of Eq. (15), i.e. Eq. (15) connects the direct CI method (the σ vector, Eq. (19), appears on the right side of Eq. (15) and is expressed via Eq. (11)) with the diagonalization methods for large matrices as required by the CI eigenvalue problem.

CALCULATION OF MOLECULAR PROPERTIES BY CI

A quantum chemical method will be considered to be ready for routine use if first- and second-order response properties can be routinely calculated. This is greatly aided by the derivation and programming of analytical first and second energy derivatives. In 1980, two back-to-back papers reported the analytical derivation of the CI gradient. Brooks and co-workers⁵⁵ based their derivation on the loop-driven GUGA CI, which provided a computationally feasible way for obtaining the two-particle density matrix and expressing the CI-gradient in terms of the latter, the one-particle density matrix, the derivatives of the molecular integrals, and the Lagrangian matrix needed in connection with the changes in the HF orbitals.

The approach of Krishnan and co-workers⁶⁰ focused on the CISD gradient, for which an explicit analytical expression in terms of integral derivatives, the first-order changes of the HF orbitals, and the CI expansion coefficients were derived. The analytical calculation of the CI gradient reduced the computational costs of the previously numerical calculations significantly, so that routine calculations of molecular geometries, dipole moments, and other first order response properties became possible at the CISD level of theory.

The Schaefer group was actively involved in the development of first and second derivatives for the CI and MR-CI energies and summarized their experience in 1994 in a monograph⁶¹ that contains all formulas for determining the analytic energy gradient and Hessian matrix. These are needed in connection with the calculation of the molecular forces (to carry out geometry optimizations) or for the calculation of molecular vibrational frequencies, which in turn are needed for the characterization of stationary points of the potential energy surface, the determination of the zero-point energy and other thermochemical

corrections or for the analysis of vibrational spectra. Another summary on this topic was given by Shepard.⁶²

THE SIZE-EXTENSIVITY PROBLEM

The size extensivity of a given quantum chemical method guarantees that the energy calculated for an electronic system with this method scales linearly with the number N of electrons. In thermodynamics, a property is called extensive if it is additive for independent, noninteracting subsystems whereas an intensive property does not depend on the size of the system considered (e.g., the temperature is the same for a system and all its subsystems). Since the energy of an electronic system is an extensive property, quantum chemical methods must describe it in this way.

The term size consistency^{63,64} is used in the case of chemical reactions, for example, when the subsystems are separated to infinitely large distance in the course of a bond-breaking reaction (dissociation) leading to two fragments of a molecule. In so far, the property of size consistency can be considered as a special case of size extensivity. However, size consistency is often also considered to imply the correct description of the dissociation products. On this basis, restricted HF (RHF) is size extensive, however not size consistent because it fails to describe homolytic dissociation (yielding two radicals for single bond dissociation) correctly whereas unrestricted HF (UHF) is both size extensive and size consistent.

It was Pople⁶³ who pointed out that CID and CISD are not size consistent (and also not size extensive). For a reaction $AB \rightarrow A + B$, described with the CID method, the products are calculated separately so that the sum of product energies effectively contains disconnected Q excitations and is much better described than the reactant AB , for which just D excitations are used. In this way, an endothermic (exothermic) reaction energy is underestimated (overestimated). The property of size consistency can be checked in the following way:

If two noninteracting systems A and B are calculated as a supersystem $\{A \cdots B, 10\}$ (e.g., with a distance of 10 Å between A and B), then the sum of the energies $E(A) + E(B)$ must fulfill the following condition:

$$E(A \cdots B, 10) = E(A) + E(B) \quad (20)$$

within numerical accuracy. This condition is fulfilled by any truncated coupled cluster (CC) method; however, truncated CI methods do not fulfill the condition due to the lack of size consistency although

size-consistency errors become rapidly smaller with increasing length of the CI expansion. Only FCI fulfills the requirements of size extensivity and size consistency.

The deficiencies of truncated CI have been traced back to product terms in the CI projection equations where both parts of a product scale with N and accordingly the product with N^2 . These terms correspond to unlinked diagrams in the diagrammatic representation of the theory. The appearance of unlinked diagrams is in itself not problematic as long as the unlinked diagrams are canceled out by other unlinked diagrams in the projection equations. This is the case for truncated CC methods, which fulfill the *linked diagram theorem*,⁶⁵ whereas the truncated CI methods fail to do so.

There have been numerous methods to remedy the size-extensivity problem of truncated CI. Best known is the Langhoff–Davidson correction,⁶⁶ that is based on the energy of a CID calculation.

$$\begin{aligned} \Delta E(LD) &= [E(CID) - E(HF)](1 - c_0^2) \\ &= \Delta E(CID, corr)(1 - c_0^2) \end{aligned} \quad (21)$$

where $\Delta E(LD)$ gives the size-extensivity correction, $E(CID) - E(HF)$ is the CID correlation energy $\Delta E(CID, corr)$, and c_0 is the coefficient of the HF reference in the CI expansion. It is common to apply the same formula also for CISD calculations or to use improvements of it in form of the renormalized Davidson (RD) correction⁶⁷

$$\Delta E(RD) = \Delta E(CID, corr) \frac{1 - c_0^2}{c_0^2} \quad (22)$$

the Davidson–Silver correction,⁶⁷ the Pople correction,⁶⁴ or a more elaborate form by Duch and Diercksen.⁶⁸ Using fourth-order many-body perturbation theory (MBPT), Barlett and Shavitt⁶⁹ showed that the Langhoff–Davidson correction⁶⁶ accounts for the correlation effects of unlinked quadruple excitations, which is a major part of the size-extensivity error of CID and CISD.

Another way of correcting for the size-consistency error of truncated CI has been worked out by Ahlrichs and co-workers⁷⁰ who related the CISD approach to the coupled electron pair approximation CEPA-1 and developed the coupled pair functional (CPF) approach. CPF is based on a correct description of separated electron pairs and uses invariance requirements with regard to unitary transformations of equivalent orbitals of identical subsystems. It introduces products of S and/or D excited terms, which cancel out some of the higher unlinked excitation terms of a truncated CI expansion.

Size-extensivity and size-consistency corrections can be useful. They are best documented for D excited configurations, whereas there is a lack of correction possibilities for S and T excited configurations (note that when correcting CISD energies, one assumes that the S excitations make only a minor contribution to size-extensivity error, which is not always justified). Also, there is no generally applicable way of correcting size-extensivity errors for other properties than the energy. Size-extensivity problems of the truncated CI can be partly cured when choosing a MR–CI method.

Duch and Diercksen⁶⁸ have pointed out that quantum mechanics is a holistic theory and accordingly does not provide a well-defined way of describing subsystems. In view of this fact, they consider size extensivity as not the most important property of a quantum chemical method. If the lack of size consistency is approximately corrected, the method is considered still valuable as long as it can describe the dissociation channels of a chemical system correctly.

MODERN USE OF CI METHODS

CISD calculations improved by the Langhoff–Davidson or other similar, approximate corrections have been used in the 1970s and 1980s, however were soon replaced by the more economic (nonvariational) MBPT and more accurate CC methods. Yet, this did not stop the development of new CI methods. Harrison and Handy⁷¹ found on the basis of FCI calculations that CISD recovers 95–96% of the total correlation energy determined with a specific basis set. The addition of T excitations (CISDT) approximately accounts for an additional 1% of the total correlation energy, whereas the addition of all quadruples (CISDTQ) recovers more than 99%.

Various attempts were made to include T and Q excitations in an approximate or indirect way.⁷² Sherill and Schaefer⁷³ were the first to solve the $O(M^{10})$ problem of CISDTQ in an efficient way by choosing the natural spin orbitals of a CISD calculation and using them to identify those classes of T- and Q-substituted configurations, which deemed most important in view of the natural orbital populations. Their results for a cc-pVTZ basis set description of water show impressively how the number of Slater determinants increases from CISD to CISDT and CISDTQ: 15,939; 938,679; 28,085,271.⁷³ In 2006, Bunge and Carbo-Dorca⁷⁴ carried out a CISDTQ calculation of the ground state of the Ne atom using a 12s12p11d10f10g9h8i7k6l5m4n3o3q3r (!) basis set and applying a selected divide-and-conquer

algorithm. The dimension of the CSF space was 1.4×10^9 and involved more than a trillion distinct Slater determinants. Hence, teraflops computing makes these computation possible and provides a possibility for these highly correlated configuration interaction calculations.⁷⁵

CI methods have retained their importance for quantum chemistry in form of FCI and MR-CI approaches. FCI is an approach that guarantees that all errors are removed from the N -electron space so that the accuracy of the one-electron basis set can be assessed. This was first emphasized already in 1981 by Saxe et al.⁷⁶ who solved the first 1 million-dimensional FCI eigenvalue problem. In the 1980s, new methods for solving the FCI problem were developed where especially the work by Knowles and Handy,⁷⁷ Siegbahn,⁷⁸ and Olsen and co-workers⁷⁹ has to be mentioned. Bauschlicher and Taylor⁸⁰ carried out FCI benchmark calculations having matrix dimensions up to 28 millions. Knowles and Handy⁸¹ reported FCI calculations with 210 million Slater determinants. An impressive breakthrough was accomplished when Olsen et al.⁸² presented the FCI description of the Mg atom, which for 10 active electrons and 30 active orbitals required the solution of a 1 billion-dimensional eigenvalue problem (1,016,018,176 Slater determinants).

In the past decade, FCI benchmark calculations with more than 10 billion determinants have been carried out, for example, for the N_2 molecule⁸³, the CN anion,⁸⁴ or different states of the diatomics BN and AlN.⁸⁵ One of the largest FCI calculation done so far seems to be the investigation of C_2 based on 65 billion Slater determinants.⁸⁶

Most of the FCI methods developed in the past three decades are based on the use of Slater determinants rather than CSFs because the coupling coefficients for Slater determinants can only be 0 or ± 1 . There is however still the need for using CFSs because of the troubling input–output bottleneck of the FCI eigenvalue problem. Tens to hundreds of terabytes of disk space are needed to store the expensive parts for the iterative calculation of the direct CI vector σ . This number can be significantly reduced when using CSFs because the FCI matrix contains in this case a lower number of nonzero elements. Further progress can be expected by exploiting the sparse nature of the FCI expansion vector (sparse FCI) with the aim of avoiding extensive disk reading/writing operations. The basic idea of these approaches is to avoid the treatment of unimportant determinants in the expansion vector c when performing the linear transformation $\sigma = Hc$ (see, e.g., Rolik and co-workers⁸⁷).

The huge FCI calculations done in recent years are of course a result of the adaptation of the FCI algorithm to parallel computer architectures and the extensive use of powerful supercomputers. Further progress can be expected with the advent of petaflops computing.

COMPARISON OF THE CONFIGURATION INTERACTION AND COUPLED CLUSTER METHODS

CI and CC theory are closely related to each other in so far as the FCI and full-coupled cluster (FCC) approach both lead to the exact wavefunction and the exact energy for an N -electron system described with a given basis set of finite size (i.e., the term *exact* refers to the one-particle basis used):

$$|\Psi\rangle = \hat{C}|\Phi_0\rangle = \exp(\hat{T})|\Phi_0\rangle \quad (23)$$

where \hat{C} and \hat{T} are the CI and CC excitation operators, respectively, defined in the following way:

$$\hat{C} = 1 + \sum_p^n \hat{C}_p \quad (24)$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_n \quad (25)$$

with

$$\hat{T}_1|\Phi_0\rangle = \sum_{i,a} t_i^a |\Phi_i^a\rangle \quad (26)$$

$$\hat{T}_2|\Phi_0\rangle = \sum_{i>j,a>b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (27)$$

$$\hat{T}_3|\Phi_0\rangle = \sum_{i>j>k,a>b>c} t_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle \quad (28)$$

All \hat{T}_n contributions are connected and lead to the representation of n -electron correlation effects, i.e., the correlation of n electrons at the same time. Already for three electrons, there is a small probability of a simultaneous correlated movement and accordingly the connected three-electron correlation energies are small. However in view of the fact that there is a large number of such connected three-electron correlations, the total of all \hat{T}_3 correlation contributions can represent an important part of the molecular correlation energy, especially if molecules with electron-rich or strongly electronegative atoms, multiple bonds, or electron delocalization are investigated. There is an even lower probability that connected four-electron correlations take place. Their total contribution to

the electron correlation energy is normally less than 1%.

In view of the exponential form of the CC wave function, there are also a large number of nonlinear cluster terms^{16,17,88}

$$|\Psi_{CC}\rangle = \exp(\hat{T})|\Phi_0\rangle \\ = (1 + \hat{T} + \hat{T}^2/2 + \hat{T}^3/3! + \dots)|\Phi_0\rangle \quad (29)$$

which lead to disconnected, but still linked contributions to the exact wavefunction involving products of the cluster operators such as $\hat{T}_1\hat{T}_1$, $\hat{T}_1\hat{T}_2$, $\hat{T}_2\hat{T}_2$. Considering that S excitations lead to an improvement of orbitals under the impact of dynamic electron correlation, these contributions correspond to independent orbital rotations, an orbital rotation taking place at the same time with pair correlation, independent pair-pair correlations, etc.

The CI excitation operators \hat{C}_p contain effects of the connected cluster operator \hat{T}_p plus all nontrivial partitions of \hat{T}_p in products of disconnected cluster operators:

$$\hat{C}_1 = \hat{T}_1 \quad (30)$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \quad (31)$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 \quad (32)$$

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4 \quad (33)$$

Hence, a pattern of the different electron correlation effects emerges out of the cluster decomposition of the electronic wavefunction. It is easy to foresee which correlation effects are more important than others. For example, pair-pair correlation effects represented by $1/2\hat{T}_2^2$ are more important than the connected four-electron correlation effects associated with \hat{T}_4 .

The advantages and disadvantages of CI and CC theory become obvious when truncating the CI or CC expansion. In view of the discussion given above, these can be summarized as follows:

1. Truncated CI is variational and yields an upper bound to the true energy. Truncated CC is not variational, which could be considered as a disadvantage. However, practice has shown that the variational property of a wavefunction is less important than the size extensivity of calculated energies and other properties.

- Truncated CI describes dynamic (short-range) electron correlation and for truncation at the T and Q level still a significant amount of non-dynamic (long-range) electron correlation, for example, caused by a (quasi)degeneracy of electronic states. Truncated CC methods account for dynamic and also some nondynamic electron correlation effects, however, fail in the case of degeneracy of the reference $|\Phi_0\rangle$. Truncated CC has the advantage of incorporating important disconnected correlation effects at a much lower level than CI as will be shown in the following.
- Truncated CI can be extended to a MR version without serious conceptual problems. This however is much more difficult in the case of CC theory although a huge amount of work has been done in this direction.^{17,89}
- Truncated CI suffers from the fact that it is no longer size extensive, whereas truncated CC is. For example, the CCD method would lead to the following wavefunction:

$$|\Psi_{CCD}\rangle = \exp(\hat{T}_2)|\Phi_0\rangle \\ = \left(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \dots\right)|\Phi_0\rangle \quad (34)$$

which indicates that for both reactant and products the disconnected pair–pair (described by \hat{T}_2^2), pair–pair–pair correlation effects (described by \hat{T}_2^3), etc. are all included thus fulfilling the condition given by Eq. (20) in the way that the same correlation effects are assessed for reactant and products. This property of truncated CC is most important for the studies of molecules and chemical reactions and makes therefore CC theory superior to CI theory. CISD energies, which are corrected with the help of the Langhoff–Davidson correction⁶⁶ or other correction schemes, are denoted as CISD+Q energies, $E(\text{CISD} + Q)$.

$$\Delta E(\text{CISD} + Q) = E(\text{CISD}) + (1 - c_0^2)\Delta E(\text{CISD}) \quad (35)$$

Since these corrections do not lead to precise size extensivity, Pople and co-workers⁹⁰ developed a more systematic improvement of truncated CI methods, which will be discussed in the following.

THE QUADRATIC CONFIGURATION INTERACTION APPROACH: MOTIVATION AND CRITICISM

J. Pople was not only a brilliant quantum chemist, but also he was perfectly capable of *selling* new methods of the Pople-group to the community of quantum chemists in an effective way. He had two successful approaches in this connection. The first was via an efficient advertisement strategy at international conferences and the second by making new methods readily available via the *Gaussian* program package.^{37,91}

Pople and co-workers⁹⁰ derived QCI methods from the corresponding CI methods with the objective of fulfilling two conditions: (i) size extensivity and (ii) correctness for two electrons where CISD represents the FCI solution. Therefore, the first QCI method started from CISD and included all S and D excitations (QCISD), was formulated for a UHF reference (to guarantee size consistency for dissociation reactions), and was described as the first size-extensive (size-consistent) CI approach, which performed in most cases as well as CCSD, however was faster and easier to apply (especially because it became soon available via the Gaussian program package).⁹⁰ In the first paper from 1987, the relation of QCISD to CCSD theory was discussed and its corrections for T substitutions via a perturbative approach was outlined, thus leading to QCISD(T), the QCI analogue of CCSD(T).⁹² Both QCI procedures were tested by application to some small electronic systems for which FCI results were available.

In the following years, Pople and/or his co-workers rapidly published several QCI applications for computationally challenging electronic systems such as ozone,⁹³ the excitation and ionization energies of transition metal atoms,^{94,95} fluorine peroxide,⁹⁶ and the bond dissociation energies (BDEs) of a variety of small molecules.⁹⁷ These studies illustrated the usefulness of the QCI approach. Especially, with the study of BDEs a long-term project of the Pople group was started, which closely connected QCI and the *Gn* (*Gaussian*) theory. The *Gn* studies led to a series of subsequent publications on thermochemical data, in which QCI played an essential role and thus guaranteed the visibility and use of QCI. For three generations of *Gn* methods, QCISD(T) was the basic tool for determining high-order correlation effects. Finally, in 2007, CCSD(T)⁹² replaced QCISD(T) as a method of choice for high-order correlation corrections in G4.⁹⁸

Additional proof for the usefulness of QCI was provided by the Cremer group. Gauss and Cremer developed in the years 1988 and 1989 the analytical energy gradients of QCISD⁹⁹ and QCISD(T)^{100,101}

where these developments were based on their previous work on the gradients for third- and fourth-order Møller–Plesset (MP3=MBPT3 and MP4=MBPT4) perturbation theory.^{102,103} (Note that we use in this review the terms MP and MBPT synonymously.) Cremer and co-workers demonstrated the usefulness of QCI when calculating QCI response properties (electron density distributions, atomic charges, dipole moments, quadrupole moments) for 20 small molecules¹⁰⁴ or the electric field gradients and nuclear quadrupole coupling constants of isonitriles.¹⁰⁵ These authors emphasized that QCI could be used for getting suitable reference values when testing the accuracy and reliability of MPn results for low values of order n .

At various conferences in the late 1980s, criticism was raised with regard to the usefulness of the QCI approach of Pople and co-workers. These concerns were first summarized in a 1989 publication of Paldus and co-workers¹⁰⁶ and triggered a scientific dispute in form of several back-and-forth *Comments* and *Replies*.^{107–109} Paldus and co-workers pointed out that QCISD, when analyzing its cluster contributions in terms of low-order perturbation theory, is very close to CPMET(C) (coupled pair many-electron-theory)¹¹⁰ or CCSD-1¹¹¹ and therefore should be considered as a CC method. Pople and co-workers¹⁰⁷ confirmed this but replied that the second of their two conditions (correctness for a two-electron system) was not fulfilled by either CPMET(C) or CCSD-1 and that the latter methods differed from QCISD by an additional $1/2\hat{T}_1^2$ term.

A more serious concern raised by Paldus and co-workers¹⁰⁶ was the fact that QCISDT, when constructed in the same way as QCISD, was no longer size extensive (size consistent). Again, Pople and co-workers¹⁰⁷ agreed with regard to this point, however pointing out that they never had claimed that it would be. Their development⁹⁰ focused on QCISD and QCISD(T), and both methods were size extensive.

There was additional controversy with regard to the reliability of QCISD as compared to CCSD and the use of the term *quadratic CI* for a method that was essentially a CC method. Pople and co-workers argued that, because of the omission of certain cluster terms in the CCSD equations, QCISD was not necessarily the less reliable method. They showed also that the QCISD equations could be derived from the FCI equations thus stressing that the name of their method was a reasonable descriptive of the derivation of QCI from FCI.¹⁰⁷

Another round of *Replies*^{108,109} did not lead to any substantial change in the arguments. It is noteworthy in this connection that Paldus and co-workers

thanked not less than 19 well-known colleagues for valuable comments and suggestions for their Reply. This indicated that more criticisms on QCI were about to be published.

Scuseria and Schaefer¹¹² published in 1989 an article, in which they demonstrated that the computational costs for both CCSD and QCISD are proportional to $O(M^6)$ and that the terms to be deleted in CCSD to obtain QCISD scale as $O(M^5)$. If suitable intermediate arrays are formulated, the algebraic equations of both approaches lead to similar calculational loads. In a 1989 feature article on CC theory, Bartlett⁸⁸ mentioned QCI shortly and stated that QCI is an approximate CC method and that the choice of the term *quadratic CI* is unfortunate because QCI contrary to CI is not based on an eigenvalue equation, nor is it variational, nor does it include all quadratic terms at the QCISD level. In an article from 1995, Bartlett and co-workers¹¹³ reported a serious failure of QCISD and QCISD(T) as compared to CCSD and CCSD(T), respectively, when calculating spectroscopic and electric properties of BeO in its GS. The authors traced back the failure of QCI to the S excitation cluster operator \hat{T}_1 , as several terms involving \hat{T}_1 are neglected in the QCISD approach contrary to CCSD.

He and Cremer^{114,115} compared CC and QCI methods in terms of sixth, seventh, eighth, and infinite-order MP perturbation theory. They determined how many of the S, D, T, Q, P (pentuple), H (hextuple) excitations are accounted for by a given QCI or CC method. Figures 1–3 summarize their results in terms of sixth order MP (MP6) theory.^{116,117} The analysis revealed that CCSD and QCISD are equivalent in the truncated space of S, D, Q, H, ... X excitations, where X is any even excitation generated by the cluster operator \hat{T}_2^m . Since these excitations describe orbital relaxation and electron pair correlation effects, which are the most important correlation effects for relatively small closed-shell molecules with just single bonds, it became understandable that QCISD and CCSD perform equally well in these cases.

However for larger molecules and for molecules with distinct T effects, CCSD outperforms QCISD because of the following three reasons: (i) QCISD rapidly falls back behind CCSD at higher values of n with regard to the total number of energy contributions covered (Figures 1 and 2). (ii) Part of the T, P (pentuple), ... Y contributions (Y is any odd order excitation) generated by the cluster operators $\hat{T}_1\hat{T}_2$ are delayed at the QCI level by one order of perturbation theory since they have to be introduced by S excitation coupling. (iii) Another part of the T, P, ... Y

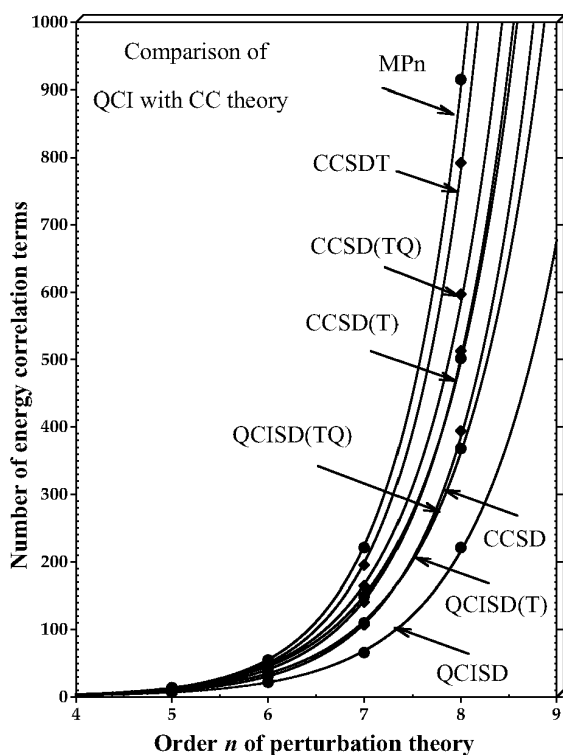


FIGURE 1 | Number of energy contributions $E^{(n)}(ABC\dots)$ accounted for by QCI, CC, and MPn ($n = 4, 5, 6, 7, 8, \dots$) methods, where A, B, C, \dots denote S, D, T, Q, \dots contributions, respectively.

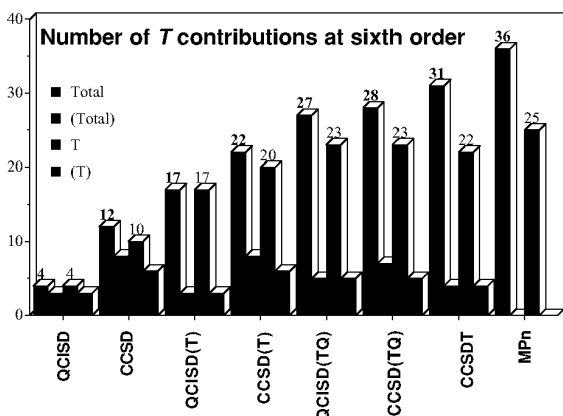


FIGURE 2 | Total number of MPn ($n = 6$) energy contributions $E^{(n)}(ABC)$ (Total: black) and number of MPn ($n = 6$) energy contributions $E^{(n)}(ABC)$ containing T effects (T: blue) as accounted for by QCI and CC methods. Some of these terms are only contained partly: (Total) in red; (T) in pink. In each case, the number of terms is given at the top of the bar (all terms) or the base of the bar (partly contained terms). Note that $MP6$ is the reference defining the total number of $E^{(n)}(ABC)$ contributions (36) as well as the total number of T contributions (25). Reproduced with permission from Ref. 118 (Copyright 1994, Springer) and Ref. 119 (Copyright 1997, Springer).

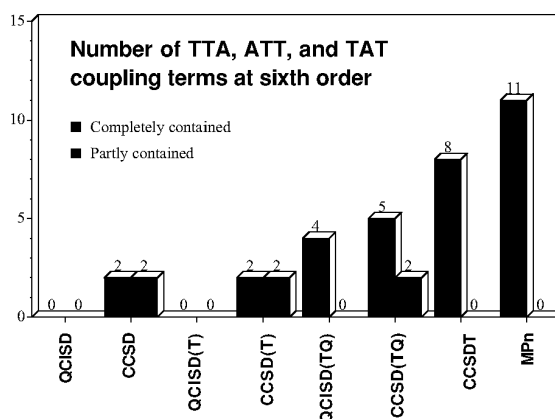


FIGURE 3 | Number of MPn ($n = 6$) energy contributions of the TTA, TAT, and TTT ($A = S, D, Q, P$) coupling type as accounted for by QCI and CC methods. The first entry (black) gives the total number, whereas the second entry (red) gives the number of terms only partly contained. Note that $MP6$ is the reference defining the total number of TT coupling contributions (11).

contributions accounted for by CCSD is not contained in QCISD at all.^{114,115}

A noniterative improvement of QCISD by T excitations is more important for QCISD than for CCSD. However, QCISD(T) exaggerates T effects since it does not contain any of the TT coupling terms (see Figure 3), which normally reduce the influence of connected three-electron correlation effects. As for the total number of energy contributions, QCISD(T) falls back behind CCSD at higher orders of perturbation theory (Figure 1). CCSD(T) is clearly the better method because it contains, at least partly, two of the TT coupling effects at sixth order. QCISD(T) easily tends to an exaggeration of T effects.

The difference between QCI and CC is considerably decreased at the CCSD(TQ) and QCISD(TQ) level of theory if one considers in particular $MP6$ correlation effects (Figure 2). However, if one considers the total number of energy contributions covered for larger n , then QCISD(TQ) is even inferior to CCSD(T) and CCSD (Figure 1). He and Cremer¹¹⁵ concluded that the superior performance of the CC methods should become obvious for any molecular system for which T effects play an important role.

ENFORCING SIZE EXTENSIVITY FOR THE QUADRATIC CONFIGURATION INTERACTION APPROACH

People never derived a QCISDT method, as a matter of fact he emphasized that it was never his objective to generalize QCISD to higher excitation

levels.¹⁰⁷ However in 1990, he and his group did publish a QCISD(TQ) method in connection with his work on fifth-order Møller–Plesset perturbation theory (MP5).¹²⁰

In view of the controversial discussion of the question whether the QCI approach could in general lead to size-extensive CI methods, the Cremer group^{118,119,121–123} analyzed truncated CI methods and, under consideration of the procedure Pople and co-workers had used for QCISD,⁹⁰ converted them into size-extensive methods. They demonstrated that QCI is not an independent method because QCID and QCISDTQ are identical with the corresponding CC methods CCD and CCSDTQ, respectively, whereas size-extensive QCISDT is neither identical with CCSDT nor with a QCISDT method derived according to Pople's concept of converting CI into size-extensive QCI.¹¹⁸ Their derivation of size-extensive CI (ECI) methods provides an insight into the basic equations of the various methods and is shortly sketched here.

In the following, CI and CC excitation operators are not distinguished by using different symbols (e.g., \hat{C} and \hat{T}). Instead, a distinction is made by denoting CI amplitudes by $c_{ijk\dots}^{abc\dots}$ and CC (QCI, ECI) amplitudes by $a_{ijk\dots}^{abc\dots}$. The operators \hat{b}^+ and \hat{b} are creation and annihilation operators.

The CID projection equations can be written as

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CID} \quad (36)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_2) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CID}, \quad (37)$$

in which \hat{H} denotes the normal-order Hamiltonian

$$\hat{H} = \hat{H} - E(HF) = \hat{H}_0 + \hat{V} \quad (38)$$

$$= \sum_{rs} \{\hat{b}_r^+ \hat{b}_s\} \langle r | \hat{F} | s \rangle + \frac{1}{4} \sum_{rstu} \{\hat{b}_r^+ \hat{b}_s^+ \hat{b}_u \hat{b}_t\} \langle rs || tu \rangle \quad (39)$$

E_{corr}^{CID} corresponds to the CID correlation energy

$$E_{corr}^{CID} = E(CID) - E(HF). \quad (40)$$

In Eq. (37), $c_{ij}^{ab} E_{corr}^{CID}$ corresponds to a disconnected term that leads to unlinked diagrams. Hence, the CID method is not size extensive. The simplest matrix element that contains the same unlinked diagrams is $\langle \Phi_{ij}^{ab} | \hat{H} \hat{T}_2^2 / 2 | \Phi_0 \rangle$. By inserting this term on the left side of Eq. (37), size-extensive CID (denoted as ECID) is obtained:

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECID} \quad (41)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECID} \quad (42)$$

Equations (41) and (42) are nothing else than the CCD equations. Hence, converting CID into size-extensive QCID by adding a quadratic cluster term directly leads to CCD, which was first noted by Pople and co-workers.⁹⁰ An independent QCID method does not exist.

The CISD projection equations are given by Eqs. (43)–(45):

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISD} \quad (43)$$

$$\langle \Phi_i^a | \hat{H}(\hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle = c_i^a E_{corr}^{CISD} \quad (44)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_1 + \hat{T}_2) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISD} \quad (45)$$

The unlinked diagrams result now from $c_i^a E_{corr}^{CISD}$ and $c_{ij}^{ab} E_{corr}^{CISD}$ in Eqs. (44) and (45). They can be canceled by adding $\langle \Phi_i^a | \hat{H} \hat{T}_1 \hat{T}_2 | \Phi_0 \rangle_D$ (subscript D denotes the disconnected part) on the left of Eq. (44) and $\langle \Phi_{ij}^{ab} | \hat{H} \hat{T}_2^2 / 2 | \Phi_0 \rangle$ on the left of Eq. (45). In this way, the ECISD (size-extensive CISD) projection equations are obtained.

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISD} \quad (46)$$

$$\langle \Phi_i^a | \hat{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle = a_i^a E_{corr}^{ECISD} \quad (47)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle = a_{ij}^{ab} E_{corr}^{ECISD} \quad (48)$$

ECISD is identical to QCISD; however contrary to QCID, QCISD is not identical to the corresponding CC method, CCSD.¹¹⁸

The CISDT projection equations are given by Eqs. (49)–(52)

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISDT} \quad (49)$$

$$\langle \Phi_i^a | \hat{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_i^a E_{corr}^{CISDT} \quad (50)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISDT} \quad (51)$$

$$\langle \Phi_{ijk}^{abc} | \hat{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_{ijk}^{abc} E_{corr}^{CISDT}. \quad (52)$$

From Eqs. (50) and (51), the ECISDT projection equations for S and D excitations are obtained in the same way as the corresponding ECISD equations.

The T projection equation contains two disconnected terms: $\langle \Phi_{ijk}^{abc} | \hat{H} \hat{T}_1 | \Phi_0 \rangle$ and $c_{ijk}^{abc} E_{corr}^{ECISDT}$. The latter term can be cancelled by applying $\hat{T}_2 \hat{T}_3$ on the left side of Eq. (52). However by canceling $c_{ijk}^{abc} E_{corr}^{ECISDT}$, one gets the new disconnected term $\langle \Phi_{ijk}^{abc} | \hat{T}_2 (\hat{H} \hat{T}_3)_c | \Phi_0 \rangle = \sum_s^S \langle \Phi_{ijk}^{abc} | \hat{T}_2 | \Phi_s \rangle \langle \Phi_s | (\hat{H} \hat{T}_3)_c | \Phi_0 \rangle$, where the subscript c denotes a restriction to connected terms. This requires the inclusion of further terms for which the single excitations multiplied by \hat{T}_2 and the double excitations multiplied by \hat{T}_1 are used thus leading to the extra terms $\hat{T}_1 \hat{T}_2$, $1/2 \hat{T}_1 \hat{T}_2^2$, $1/2 \hat{T}_1^2$, and $\hat{T}_1 \hat{T}_3$. In this way, all disconnected terms are cancelled in Eq. (52) and size extensivity is enforced.¹¹⁸ This leads to

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{ECISDT} \quad (53)$$

$$\begin{aligned} \langle \Phi_i^a | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle \\ = a_i^a E_{corr}^{ECISDT} \end{aligned} \quad (54)$$

$$\begin{aligned} \langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle \\ = a_{ij}^{ab} E_{corr}^{ECISDT} \end{aligned} \quad (55)$$

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2} \hat{T}_1^2 \\ + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_1 \hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle \\ = (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 \rangle) E_{corr}^{ECISDT} \end{aligned} \quad (56)$$

or, alternatively, to

$$\langle \Phi_i^a | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_c = 0 \quad (57)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle_c = 0, \quad (58)$$

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | \hat{H} (\hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \hat{T}_2 \hat{T}_3 \\ + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_1 \hat{T}_2^2) | \Phi_0 \rangle_c = 0 \end{aligned} \quad (59)$$

i.e., when constraining to connected terms.

Clearly, *ECISDT* (size-extensive CISDT) is not identical to the *QCISDT* method constructed in the same way as *QCISD*.⁹⁰ Since *ECISDT* is also not identical to *CCSDT*, it is intermediate between *QCISDT* and *CCSDT*, but closer to the latter than the former method. *ECISDT* and *CCSDT* are both size-extensive whereas *QCISDT* is not.¹¹⁸

The CISDTQ projection equations are given by Eqs. (60) to (64):

$$\langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{corr}^{CISDTQ} \quad (60)$$

$$\langle \Phi_i^a | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_i^a E_{corr}^{CISDTQ} \quad (61)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ij}^{ab} E_{corr}^{CISDTQ} \quad (62)$$

$$\langle \Phi_{ijk}^{abc} | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ijk}^{abc} E_{corr}^{CISDTQ} \quad (63)$$

$$\langle \Phi_{ijkl}^{abcd} | \hat{H} (\hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_{ijkl}^{abcd} E_{corr}^{CISDTQ}. \quad (64)$$

Extending these equations by terms, which cancel the unlinked diagrams, the *ECISDTQ* projection equations are obtained, which turn out to be identical with the *CCSDTQ* equations:

$$E_{corr}^{CCSDTQ} = \langle \Phi_0 | \hat{H} (\hat{T}_2 + \frac{1}{2} \hat{T}_1^2) | \Phi_0 \rangle \quad (65)$$

$$\begin{aligned} \langle \Phi_i^a | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \frac{1}{3!} \hat{T}_1^3) | \Phi_0 \rangle \\ = a_i^a E_{corr}^{CCSDTQ} \end{aligned} \quad (66)$$

$$\begin{aligned} \langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_1^2 \\ + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 + \frac{1}{4!} \hat{T}_1^4) | \Phi_0 \rangle \\ = (a_{ij}^{ab} + \langle \Phi_{ij}^{ab} | \frac{1}{2} \hat{T}_1^2 | \Phi_0 \rangle) E_{corr}^{CCSDTQ} \end{aligned} \quad (67)$$

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_3 \\ + \hat{T}_1 \hat{T}_4 + \frac{1}{2} \hat{T}_2^2 + \hat{T}_2 \hat{T}_3 + \frac{1}{3!} \hat{T}_1^3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 \\ + \frac{1}{2} \hat{T}_1^2 \hat{T}_3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_4 + \frac{1}{2} \hat{T}_1 \hat{T}_2^2 + \hat{T}_1 \hat{T}_2 \hat{T}_3 + \frac{1}{3!} \hat{T}_1^3 \\ + \frac{1}{4!} \hat{T}_1^4 + \frac{1}{3!} \hat{T}_1^3 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 \hat{T}_3 + \frac{1}{4} \hat{T}_1^2 \hat{T}_2^2 \\ + \frac{1}{5!} \hat{T}_1^5 + \frac{1}{6!} \hat{T}_1^6) | \Phi_0 \rangle \\ = (a_{ijk}^{abc} + \langle \Phi_{ijk}^{abc} | \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 | \Phi_0 \rangle) E_{corr}^{CCSDTQ} \end{aligned} \quad (68)$$

$$\begin{aligned}
&\langle \Phi_{ijkl}^{abcd} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \hat{T}_1\hat{T}_3 \\
&\quad + \hat{T}_1\hat{T}_4 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_2\hat{T}_3 + \hat{T}_2\hat{T}_4 + \frac{1}{2}\hat{T}_3^2 \\
&\quad + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_4 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 \\
&\quad + \hat{T}_1\hat{T}_2\hat{T}_3 + \frac{1}{3!}\hat{T}_2^3 + \frac{1}{4!}\hat{T}_1^4 + \frac{1}{3!}\hat{T}_1^3\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3\hat{T}_3 \\
&\quad + \frac{1}{4}\hat{T}_1^2\hat{T}_2^2 + \frac{1}{5!}\hat{T}_1^5 + \frac{1}{4!}\hat{T}_1^4\hat{T}_2 + \frac{1}{6!}\hat{T}_1^6) | \Phi_0 \rangle \\
&= (a_{ijkl}^{abcd} + \langle \Phi_{ijkl}^{abcd} | \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 \\
&\quad + \frac{1}{4!}\hat{T}_1^4 | \Phi_0 \rangle) E_{corr}^{CCSDTQ} \quad (69)
\end{aligned}$$

This derivation underlines two important facts:

- A size-extensive truncated CI (ECI) method, which contains P -fold substitutions ($P = S, D, T, Q, \dots$) cannot be achieved by just considering quadratic correction terms in the two highest projection equations.
- Size-extensive ECI methods do not form a hierarchy of independent CC methods, and, therefore, the concept of improving truncated CI to size-extensive CI is not a generally useful concept. The same holds for the quadratic CI approach in the sense as it was originally derived.⁹⁰

Cremer and He¹¹⁸ used the ECI projection equations to develop a hierarchy of size-extensive CI methods for a reference wavefunction constructed from HF orbitals. Since these methods are also based on the addition of quadratic terms to the CI projection equations where however the addition is done in such a way that all disconnected terms are canceled and just connected terms remain in the new QCI projection equations, the term QCIC (c: connected) was coined.¹¹⁸ Formally, the QCIC equations can be derived directly from the corresponding CI equations. For this purpose, the projection equations of a truncated CI method that includes up to p -fold excitations are written as follows:

$$E_{corr}^{CI} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \quad (70)$$

$$\begin{aligned}
&\langle \Phi_p | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n) | \Phi_0 \rangle \\
&= c_p E_{corr}^{CI} \quad (p = 1, 2, \dots, n) \quad (71)
\end{aligned}$$

or, alternatively, as

$$\langle \Phi_s | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) | \Phi_0 \rangle = c_s E_{corr}^{CI} \quad (72)$$

$$\langle \Phi_d | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) | \Phi_0 \rangle = c_d E_{corr}^{CI} \quad (73)$$

$$\langle \Phi_p | \bar{H}(\sum_{i=p-2}^{\min[p+2,n]} \hat{T}_i) | \Phi_0 \rangle = c_p E_{corr}^{CI} \quad (n \geq p \geq 3) \quad (74)$$

where s , d , and p are S, D, and general excitation indices.

As shown above, it suffices to add $\hat{T}_1\hat{T}_2$ and $\hat{T}_2^2/2$ to the S and D projection Eqs. (72) and (73), respectively, to eliminate all disconnected terms from these equations. For any excitation index p higher than d , just the disconnected terms $\langle \Phi_p | \bar{H} \hat{T}_{p-2} | \Phi_0 \rangle$ and $c_p E_{corr}^{CI}$ appear in the corresponding projection equations. Introduction of $-\hat{H} \hat{T}_{p-2}$ and parts of the term $\bar{H} \hat{T}_2 \hat{T}_p$, namely $(\bar{H} \hat{T}_2 \hat{T}_p)_C$ and $\hat{T}_p(\bar{H} \hat{T}_2)_C$, on the left side of Eq. (74) leads to a cancellation of all disconnected terms and to the QCIC equations in their general form¹¹⁸:

$$E_{corr}^{QCIC} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \quad (75)$$

$$\langle \Phi_s | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3) + (\bar{H} \hat{T}_1 \hat{T}_2)_C | \Phi_0 \rangle = 0 \quad (76)$$

$$\langle \Phi_d | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4) + \frac{1}{2}(\bar{H} \hat{T}_2^2)_C | \Phi_0 \rangle = 0 \quad (77)$$

$$\begin{aligned}
&\langle \Phi_p | \bar{H}(\sum_{i=p-1}^{\min[p+2,n]} \hat{T}_i) + (\bar{H} \hat{T}_2 \hat{T}_p)_C | \Phi_0 \rangle \\
&= 0 \quad (n \geq p \geq 3) \quad (78)
\end{aligned}$$

These projection equations lead to a hierarchy of QCIC methods that are all size extensive.

On the basis of this approach, Cremer and He¹²¹ developed size-extensive QCISDTc:

$$E_{corr}^{QCISDT} = \langle \Phi_0 | \bar{H} \hat{T}_2 | \Phi_0 \rangle \quad (79)$$

$$\langle \Phi_i^a | \bar{H}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_2) | \Phi_0 \rangle_C = 0 \quad (80)$$

$$\langle \Phi_{ij}^{ab} | \bar{H}(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2}\hat{T}_2^2) | \Phi_0 \rangle_C = 0 \quad (81)$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}(\hat{T}_2 + \hat{T}_3 + \hat{T}_2\hat{T}_3) | \Phi_0 \rangle_C = 0. \quad (82)$$

The authors demonstrated that QCISDTc leads to results comparable to those obtained with CCSDT, which has to do with the fact that up to fifth-order perturbation theory just the TQ coupling term of MP5 is missing.¹²¹ Although QCISDTc and CCSDT both scale with $O(M^8)$ (actually $O(N^3(M - N)^5)$), the former method offers time saving because of its faster convergence in the QCIC iterations. He and co-workers¹²² showed in a follow-up publication that QCISDTc is clearly superior to QCISD(T), and they traced performance advantages back to a better description of TT coupling terms contained in the former, however not in the latter method.

In 2000, He and co-workers¹²³ extended the size-extensive QCIC methods by developing QCISDTQc:

$$E_{corr}^{QCISDT} = \langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle \quad (83)$$

$$\langle \Phi_i^a | \hat{H} (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_1 \hat{T}_2) | \Phi_0 \rangle_C = 0 \quad (84)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \frac{1}{2} \hat{T}_2^2) | \Phi_0 \rangle_C = 0 \quad (85)$$

$$\langle \Phi_{ijk}^{abc} | \hat{H} (\hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_3) | \Phi_0 \rangle_C = 0 \quad (86)$$

$$\langle \Phi_{ijkl}^{abcd} | \hat{H} (\hat{T}_3 + \hat{T}_4 + \hat{T}_2 \hat{T}_4) | \Phi_0 \rangle_C = 0 \quad (87)$$

These authors also developed QCISDTQc(6) as a size-extensive Q excitation method that is exact at sixth-order perturbation theory, leads to results which are better than those from CCSD(T), QCISDTc, or CCSDT calculations and close to CCSDTQ and FCI results. QCISDTQc(6) is the cheapest of all Q excitation containing methods accounting for infinite order correlation effects introduced by the \hat{T}_4 cluster operator. He and co-workers¹²³ also showed the importance of connected four-electron correlation effects, which especially in the case of multireference electronic systems containing electronegative atoms are needed to closely approximate FCI reference energies.

CONCLUSIONS AND OUTLOOK

The research on CI theory was for many decades one of the major driving forces for the development of accurate and routinely applicable quantum chemical methods. If the early pioneers of the CI theory had known about all the obstacles and the enormous

mathematical problems of carrying out for example a FCI calculation for just a 10-electron atom with a larger basis set, they probably would have stopped their efforts, which would have been a tremendous loss to quantum chemistry as a whole. Many of the heroic attempts to improve the performance of CI triggered activities aimed at the development of alternative methods, deepened the understanding of the quantum chemical methodology, and provided an insight into calculational outcomes.

Today, the continuous value of CI theory results from two basic facts: (i) Single reference CI discussed in this article can be easily extended to MR-CI (at least conceptually), which is the method of choice in many cases. This is more difficult for multireference CC theory.⁸⁹ (ii) There is a continuous interest in FCI calculations because of the need of reliable reference values. Also new developments such as the connection of FCI with quantum Monte Carlo¹²⁴ calculations have opened new avenues for FCI applications. However, one should not forget that a system with 12 electrons in 20 orbitals or 10 electrons in 30 orbitals already leads to a billion Slater determinants so that FCI reference calculations are rather limited.

Truncated CI is used today mostly to demonstrate the shortcomings of CI. There is however an interest in using truncated CI in connection with relativistic theory, for example, when calculating spin orbit coupling effects.¹²⁵ The situation is somewhat different for highly correlated CI methods such as CISDTQ, which leads to energies close to FCI energies and therefore is an interesting reference method. In view of the costs of a CISDTQ calculation, the use of this and similar CI methods is also rather limited.

The QCI approach is certainly closer to CC rather than CI theory. This may be disputable for the original QCISD method of Pople and co-workers.⁹⁰ However, this statement is definitely true if this approach is converted into a general, size-extensive (size-consistent) QCIC method as done by Cremer and co-workers.^{118,121-123} The original QCISD approach does not lead to a set of independent methods because converting truncated CI into Pople-type QCI methods only leads to QCISD, whereas QCID = CCD⁹⁰ and QCISDT, QCISDTQ, etc. are not size extensive (however, ECISDT, ECISDTQ, QCISDTc, and QCISDTQc are size extensive).¹¹⁸

With CCSD(T) becoming the *gold standard* for quantum chemical calculations,¹²⁶ the use of QCISD(T) has dramatically decreased. QCISD(T) does not lead to significant cost advantages, has deficiencies with regard TT coupling effects, and fails if systems with multireference character are investigated. This is also documented by the fact that the

G4-theory of Curtiss⁹⁸ is based on CCSD(T) rather than QCISD(T).

Clearly, the scientific dispute between Pople and his group on the one side and a large number of well-known colleagues headed by Paldus on the other side has been fruitful, especially with regard to realizing more clearly the problems of truncated CI methods, the importance of size extensivity, and the advantages of CC theory. Some of the scientific dispute on the usefulness of the QCI approach has reached into our days because the Gaussian series of programs started by Pople³⁷ is still heavily used today, and one of

the approximate CC methods offered in the Gaussian program is QCI. Therefore, it is not surprising that even in our time QCI is discussed and reviewed. In 2006, Bartlett and Musial¹²⁷ reconsidered the possibility of deriving truncated, but size-extensive CI methods. Paldus¹²⁶ wrote in 2010 a retrospection on QCI and the scientific dispute he had with Pople where he points out in a humorous way that the opponents of the dispute never lost their mutual respect and appreciation. Clearly, QCI is worth to be reviewed in the year 2012, but the current summary may be one of the last reviews on the topic.

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