Coupled-cluster Theory. The Evolution Toward Simplicity in Quantum Chemistry

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Perspective on: **Coupled-cluster Theory. The Evolution Toward Simplicity in Quantum Chemistry**

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Coupled-cluster theory has revolutionized quantum chemistry. It has provided the framework to effectively solve the problem of electron correlation, the main focus of the field for over 60 years. This has enabled *ab initio* quantum chemistry to provide predictive quality results for most quantities of interest that are obtainable from first-principle calculations. The best that one can do in a basis is the 'full CI,' the exact solution of the non-relativistic Schrödinger equation. or, if need be, the relativistic Dirac equation. With due regard to converging the basis set and adequate consideration of higher clusters and relativity in a calculation, virtually predictive results can be obtained. But in addition to its numerical performance, coupled-cluster theory also offers a conceptually new, many-body foundation for the theory that should be appreciated for all practitioners. The latter is emphasized in this perspective, leading to the 'Evolution Toward Simplicity' in the title. The ultimate theory will benefit from the several features that are uniquely exact in coupled-cluster theory and its EOM-CC extensions.

Forward.

The following contribution is a perspective on coupled-cluster theory, not a review. The latter has already been published in Reviews of Modern Physics[1] where most of the theory is summarized including its diagrammatic and algebraic equations with copious references, and many numerical examples presented to show the power and limitations of the theory as it appeared in 2007. Other reviews include Paldus on the early days of the theory,[2] and another in the same source on its more recent evolution.[3] This perspective instead focuses on the fundamental aspects of CC theory and its EOM-CC extensions that should be appreciated by all quantum or computational chemists— theory developers or those making applications—- with no diagrams or even extensive references to detract attention. Instead, most of the questions addressed are fundamental to the many-body formulation and understanding of modern day quantum chemistry that leads to the 'evolution toward simplicity' in the title, and that helps to point the way for future developments. An attempt has been made to make all points and derivations herein self-contained.

The latter parts of this perspective address new developments in CC/EOM-CC that have emerged since the 2007 review, that serve to further address the 'Evolution toward Simplicity' theme. These include time-dependent EOM-CC to obtain the electronic spectra of molecules from core excitations to high-lying Rydberg states, new treatments for doubly excited states that correct this well-known limitation in EOM-CCSD, some accommodations for certain multi-refererence issues and their characterization,[4] and applications to infinite systems from polymers to crystalline solids.[5] An important future application will be applying unitary CC (UCC) for quantum computers.[6,7]

A. Essentials

Quantitative quantum chemistry is a recent phenomenon. It is ultimately defined by the numerical results of a full CI (FCI) calculation in a complete basis set that is the solution of the non-relativistic Schrödinger equation. Though not achievable in practice, one can come close to this ideal by doing FCI calculations, subject to basis set extrapolations toward completeness, or perhaps, using explicit F12[8,9] methods in the FCI. Of course, this too is seldom possible for any but small problems because the FCI itself scales as $\sim M^n$ where n is the number of electrons and M is the dimension of the basis set. But nonetheless, for finite systems FCI defines an unambiguous objective for a quantitative prediction of molecular electronic structure, energetics, and spectra, that would provide results in the absence of any experimental data.

Fundamental to chemistry is the concept of molecular orbital (MO) theory, whose one-electron spin orbitals are successively occupied to define the first approximation to the electronic structure of an atom or molecule. These orbitals can be viewed as the solutions of a one-particle Schrödinger-like equation,

$$h^{eff}(1)\varphi_p(1) = \varepsilon_p \varphi_p(1) \forall p, \tag{1}$$

of which the first n spin-orbitals, i,j,k,l ...n, are considered occupied with orbital energy, ε_i, while the remainder, M-n, a,b,c,d... are unoccupied. Unspecified indices are p, q, r, s. The occupied set defines a single determinant, the simplest possible Fermionic wavefunction, while the remaining unoccupied orbitals define one particle levels that would be partly occupied by n-electrons in a FCI wavefunction. A common situation is that the occupied orbitals are doubly occupied with α and β spin, but by using spin orbitals both open and closed shells are allowed in all equations. The latter are written in terms of orbital creation operators, $\widehat{p}^\dagger$, and annihilation ones, $\widehat{p}$, (the$\widehat{}$symbol will be eliminated when there is no confusion about p and q's role as operators or indices). The excitation operators *are* naturally in normal order, $\{a^\dagger i\}, \{a^\dagger ib^\dagger j\}, ...$ Thus, for any n-electrons,

$$\Phi_0 = A(\varphi_1(1)\varphi_2(2)...\varphi_n(n)) = |0\rangle \qquad (2)$$

$$\Phi_i^a = \{a^\dagger i\}|0\rangle \qquad (3)$$

$$\Phi_{ij}^{ab} = \{a^\dagger ib^\dagger j\}|0\rangle \qquad (4)$$

$$... \qquad (5)$$

$$\Phi_{ijkl...n}^{abcd...m} = \{a^\dagger ib^\dagger j...m^\dagger n\}|0\rangle. \qquad (6)$$

Pictorially, these orbital energy levels are shown in Fig. 1, where the space of n-occupied orbitals with projector, P, consists of one determinant and Q represents the space spanned by excitations into the unoccupied, virtual orbitals.

In each category of excitation all possible electrons from occupied orbitals that can be promoted to all possible unoccupied orbitals with the same spin provide the single, $Q_{1,}$ double, $Q_{2,}$ triple, Q_3, up to the n-fold, Q_n, excitations of the full CI, that define the Hilbert space for the problem. In the most general case of open-shells, the orbitals will be 'spin-polarized' meaning there will be separate alpha and beta spin orbitals. In the following all formal expressions are written in terms of spin-orbitals as the most expedient and general approach to open and closed shells. In actual programs, these spin orbital equations are always integrated over spin to provide an $\alpha\alpha, \beta\beta$, and $\alpha\beta$ part of the equations with obvious further simplifications for closed shells. Thus, open-shell calculations are never more than three times more time consuming than a closed shell calculation.

The FCI wavefunction is then,

$$\begin{aligned}\Psi_{FCI} =& C_0\Phi_0 + \sum_{i,a} C_i^a\Phi_i^a + \sum_{ij,ab} C_{ij}^{ab}\Phi_{ij}^{ab} + \cdots + \\ & \sum_{ijk\cdots,n,abc,\cdots,m} C_{ijk...n}^{abc...m}\Phi_{ijk...n}^{abc...m}\end{aligned} \qquad (7)$$

summed over all distinct determinants, with its coefficients, $\{C_q\}$, to be determined variationally. The latter leads to the secular equation,

$$\mathbf{HC} = \mathbf{CE} \qquad (8)$$

and describes all the electronic states of the system. It offers an upper bound to the experimental ground state energy, and via the Hylleraas, Unheim, MacDonald theorem, an upper bound to each excited state in turn, guaranteeing that all states are properly non-interacting, i.e., $\langle\Psi_S|H|\Psi_T\rangle = E_S\delta_{ST}$. Of course, though FCI provides the objective, in practice, 'truncated' CI methods are used, meaning the wavefunction is limited to subsets of possible excitations like all single and double exitations, CISD, or those chosen to provide correct separation of a molecule into its fragments, or address near-degeneracies, as in MR-CISD. Such a truncation will be denoted as 'TCI' to distinguish it from FCI. Regarding the bounding property of the FCI or TCI, an upper bound to a *total energy* is far from a bound on the energy differences fundamental to chemistry that provide all observables. Even two states of the FCI, like the ground state and its first excited state, do not provide a bound on their excitation energy difference, and this will be the case for all spectroscopic properties, or heats of reaction, heats of ionization, formation, etc. So recognize that the variational principle that has been the cornerstone of the treatment of the correlation problem since the time of Hylleraas and its realization in TCI, is not a necessary condition on the theory. In fact, it can be a handicap. In this perspective, we will see many more reasons why CI methods should be avoided in quantitative electronic structure calculations.

Whereas TCI uses a linear ansatz for a wavefunction, as in Eqn. 7, but truncated, coupled cluster (CC) theory is based upon an exponential of excitation operators. The essence is that the CC wavefunction for an electronic problem is

$$\Psi_{CC} = \exp(\widehat{T})|0\rangle = \exp(1 + \widehat{T}_1 + \widehat{T}_2 + \widehat{T}_3 + ...)|0\rangle \qquad (9)$$

where the T operator puts in single excitations, $\widehat{T}_1 = \sum t_i^a \mathrm{a}^\dagger i$, doubles $\widehat{T}_2 = \frac{1}{4}\sum t_{ij}^{ab} a^\dagger ib^\dagger j$, triples $\widehat{T}_3 = \frac{1}{6}\sum t_{ijk}^{abc} a^\dagger ib^\dagger jc^\dagger k$, ...etc. In particular, for the FCI which can be written as

$$\Psi_{FCI} = [C_0 + C_i^a a^\dagger i + C_{ij}^{ab} a^\dagger ib^\dagger j + ...]|0\rangle = [C_0 + \widehat{C}_1 + \widehat{C}_2 + \widehat{C}_3 + ...]|0\rangle \qquad (10)$$

with summation over repeated indices, the exponential provides a cluster representation and decomposition,

$$\widehat{C}_1 = \widehat{T}_1 \qquad (11)$$

$$\widehat{C}_2 = \widehat{T}_2 + \widehat{T}_1^2/2 \qquad (12)$$

$$\widehat{C}_3 = \widehat{T}_3 + \widehat{T}_1\widehat{T}_2 + \widehat{T}_1^3/3! \qquad (13)$$

$$\widehat{C}_4 = \widehat{T}_4 + \widehat{T}_2^2/2 + \widehat{T}_1\widehat{T}_3 + \widehat{T}_1^2\widehat{T}_2/2 + \widehat{T}_1^4/4! \qquad (14)$$

$$... \qquad (15)$$

In intermediate normalization as chosen here, $C_0 = 1$. The exponential operator immediately provides the result that the wavefunction of N local units, A, B, C,..., such as a cluster of separated water molecules or a collection of localized electron pair bonds is decomposed into N pieces, provided the vacuum $|0\rangle = |0_A\rangle\,|0_B\rangle\,|0_C\rangle\cdots$

$$\begin{aligned}\exp(\widehat{T})|0\rangle &= \exp(\widehat{T}_A + \widehat{T}_B + \widehat{T}_C + ...)|0_A0_B0_C....\rangle \\ &= \exp(\widehat{T}_A)|0_A\rangle\exp(\widehat{T}_b)|0_B\rangle\exp(\widehat{T}_C)|0_C\rangle...\end{aligned} \qquad (16)$$

As the exact, or FCI wavefunction , is invariant to any orbital transformation, the condition of locality is easy to enforce by orbital transformations.. The product condition on the Fermi vacuum, $|0\rangle = |0_A0_B0_C\rangle\cdots$ could be ensured by a lattice of non-

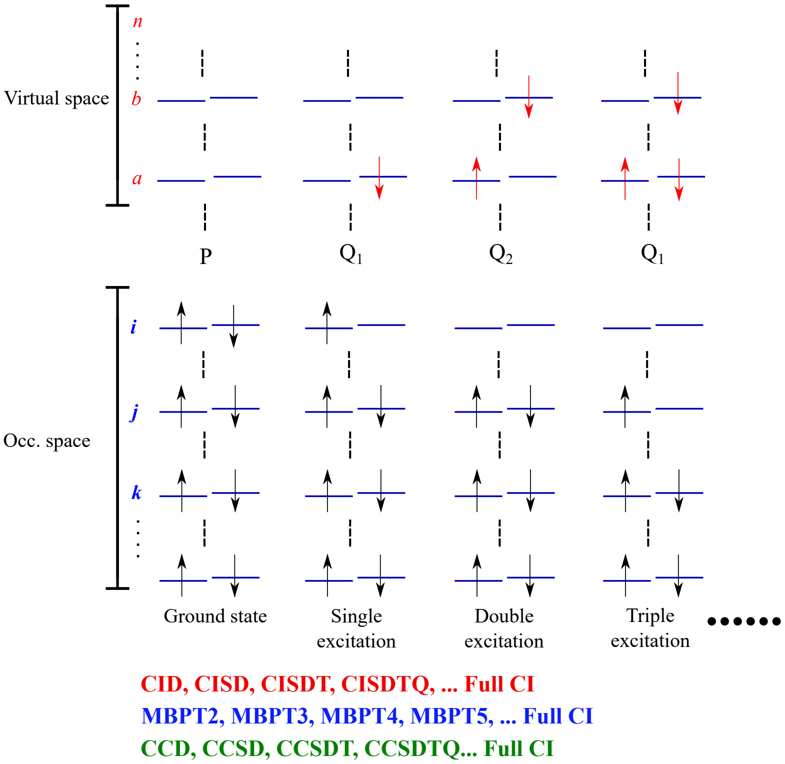


Fig. 1 Depiction of selected examples describing the various excitation manifolds. Red arrows represent the excited electrons. Electrons from all possible occupied orbitals are excited into all possible unoccupied orbitals in the full CI, Q_n

interacting units or units represented by localized orbitals.

The above immediately leads to the energy obtained from left projection of the Schrödinger equation subject to intermediate normalization, $\langle 0|\exp(T)|0\rangle = 1$,

$$\begin{aligned}\langle 0|H\exp(T)|0\rangle &= E &(17)\\ &= E_A + E_B + E_C + \ldots &(18)\\ & &(19)\end{aligned}$$

being decomposed into units to accompany the wavefunction product,

$$\exp(T)|0\rangle = \exp(T_A)|0_A\rangle \exp(T_b)|0_B\rangle \exp(T_C)|0_C\rangle \ldots \tag{20}$$

When the local units are identical, one obtains for the lattice,

$$\begin{aligned} E_L &= NE_A &(21)\\ \Psi_L &= \prod_{A=1,N} \exp(T_A)|0_A\rangle = N\exp(T_A)|0\rangle &(22)\end{aligned}$$

showing linear scaling in N. The property of ‘correct’ scaling with size in electronic systems is termed ‘size-extensivity’, [10] as any ‘extensive’ property like the energy has to scale linearly with the number of units. There are few elements in electronic structure theory that are more fundamental than this condition.

Contrast this with TCI for the simple problem of a lattice of N non-interacting H_2 molecules whose energy is NE(H_2). For just two electrons, CID, is the full CI, (assume Brueckner orbitals to make single excitations vanish). Obviously, the exact wavefunction for the whole lattice should be the product of the individual CID for each H_2, but because CI wavefunctions consist of only linear terms, this product is not a CID wavefunction. It would be possible to get an exact CI solution for two H_2 molecules, four electrons, by adding CI quadruple excitations to CID. For three molecules (6 electrons) one would need hextuple excitations, and so forth. But the simplicity of these product terms hardly requires constructing the FCI. As seen above, this feature is intrinsic to CC theory, as a CCD wavefucton is the FCI for H_2, but CCD is also the FCI for all products of non-interacting H_2 wavefunctions! As the first approximation to most of chemistry is the concept of separated electron pair bonds, the relevance is apparent.

In terms of the CC wavefunction, the usual (non-unique) choice is to obtain the T amplitudes by projection of the Schrödinger equation onto the space of all necessary excitations. For CCD, this means all double excitations. While CCSD would mean all single and double excitations, continuing to CCSDT, CCSDTQ, then P and H. (Forgive me for mixing Greek and Latin but this provides a unique description through hextuple excitations.)

The CCD equations are then a set of homogeneous equations,

$$\langle \Phi_{ij}^{ab}|(H-E)\exp(T_2)|0\rangle = 0, \forall a,b,i,j \tag{23}$$

or equivalently in the ‘connected’ form, obtained by left multiplication of the Schrödinger equation by exp(-T_2) before projection onto double excitations,

$$\langle \Phi_{ij}^{ab} | \exp(-T_2) H \exp(T_2) | 0 \rangle = 0, \forall a, b, i, j \tag{24}$$

The latter tells us that the quantity,

$$\begin{aligned}\overline{H} &= \exp(-T_2) H \exp(T_2) = H + [H, T_2] + \frac{1}{2}[[H, T_2]T_2] \\ &+ \frac{1}{3!}[[[H, T_2]T_2]T_2] + \frac{1}{4!}[[[[H, T_2]T_2]T_2]T_2] \\ &= [H \exp(T)]_C \\ &= H + (HT_2)_C + (HT_2^2/2)_C + (HT_2^3/3!)_C + (HT_2^4/4!)_C\end{aligned} \tag{25}$$

consists of only *connected* terms (those that have indices in common between H and T's for second-quantized operators) as all other terms would not survive the commutators. Note also that $\overline{H}$ terminates after four T_2 operators because the electrostatic Hamiltonian only has one and two-particle terms as shown below, meaning only a four-fold commutator can survive regardless of the rank of T_n.

To evaluate the t_{ij}^{ab} contributions to $\exp(T_2)|0\rangle$, one solves Eqn. 24, using the normal-ordered H and the generalized Wick's theorem,

$$H = \sum_{p,q} f_{pq} \{p^\dagger q\} + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{p^\dagger q^\dagger s r\} + \langle H \rangle \tag{26}$$

$$W = \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{p^\dagger q^\dagger s r\}$$

$$\begin{aligned}\langle pq || rs \rangle &= \int d1 \int d2 \varphi_p^*(1) \varphi_q^*(2) (\frac{1 - P_{12}}{r_{12}}) \varphi_r(1) \varphi_s(2) \\ &= \langle pq | rs \rangle - \langle pq | sr \rangle\end{aligned} \tag{27}$$

This provides the non-linear algebraic or diagrammatic expressions for t_{ij}^{ab},shown explicitly elsewhere[1] that need not be repeated here. A useful conceptual form for the CCD equations is

$$0 = \langle \Phi_{ij}^{ab} | H + HT_2 + HT_2^2/2 | 0 \rangle_C, \forall i.j.a.b \tag{28}$$

consisting of a linear in T_2 and a non-linear term, which becomes

$$\varepsilon_{ij}^{ab} t_{ij}^{ab} = \langle ab || ij \rangle + \langle \Phi_{ij}^{ab} | WT_2 + WT_2^2/2 | 0 \rangle_C, \forall i.j.a.b \tag{29}$$

where

$$\varepsilon_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \tag{30}$$

For the common case of canonical HF orbitals where $f_{pq} = f_{pq}\delta_{pq} = f_{pp} = \varepsilon_p$ and $f_{ia} = f_{occ,virt} = 0$, this term reduces to differences of HF orbital energies. For any other orbitals, the $f_{occ,virt} = f_{ia} \neq 0$, while f_{ij} and f_{ab} have to also be retained or transformed away via a semi-canonical transformation. The former is pertinent to localized orbitals and easy to incorporate into the iterative solution as the semi-canonical transformation would undo the localization. But for other cases the semi-canonical transformation makes all equations look like the canonical orbital case, except that the f_{ia} remains as part of the perturbation with W, easily adding non-HF or general orbital corrections to CC calculations.

Because of the natural cluster decomposition of the FCI provided by the exponential wavefunction, the lead second-order term that arises from CI quadruple excitations, C_4, in CC is simply, $\frac{1}{2}T_2^2|0\rangle$. Yet, it depends on the numbers of double excitations instead of the number of quadruple excitations. That number is $\sim n^2M^2$ and its contraction with H introduces an $\sim n^2M^4$computational dependence. Taking a small problem like n=10, M=100, the ratio of C_4 evaluation to $\frac{1}{2}T_2^2$ evaluation is $\sim 10^6$. A larger problem like 100 electrons in 1000 basis functions would give $\sim 10^{10}$.

The difference between CCD and CCDQ would measure the effect of connected T_4. In some cases it is significant, but $\frac{1}{2}T_2^2$ in CCD *accounts for all terms in fourth-order Rayleigh-Schrödinger perturbation theory (RSPT4) or MBPT4 from CI quadruple excitations*. Physically, the correlation effects from such product terms are really rather simple compared to those that would require T_4. As the exponential ansatz of CC theory is simply a re-statement of the linked-diagram theorem (LDT) of Brueckner and Goldstone,[11] all terms are guaranteed to be 'linked' in diagrammatic language, as long as T is connected. But unlinked diagrams remain in any TCI approximation but are not in the FCI result and are responsible for the TCI upper bound. It is true that a full inclusion of all C_4 terms like in CISDTQ, is almost computationally equivalent to including the *connected* T_4 clusters in CCSDTQ, but not numerically because of the retention of unliked diagrams. There is no need to be intimidated about 'many-body-diagrams' that rigorously define what is meant by 'linked' and 'unlinked', and their subsets, 'connected' and 'disconnected'. See Fig. 2 for a pictorial description.

Anyone who is comfortable with RSPT can easily connect it to 'many-body perturbation theory' (MBPT), all of whose terms are defined to be 'linked' for the energy and wavefunction. It simply means that in any order of RSPT, *all possible excitations are included in the calculations, like in FCI, but now limited to a particular order; then one has MBPT*. This means MBPT2 and MBPT3 consist of only singles and double excitations, and only the latter for HF orbitals. Once one gets to MBPT4, singles, doubles, triples, and quadruples are included. But the latter comes solely from $\frac{1}{2}T_2^2$, The first appearance of connected T_4 occurs in MBPT5.

The defining equations of MBPT are usually written as

$$\Psi_{MBPT} = |0\rangle + \sum_{k=1}^{\infty} (R_0 H)^k |0\rangle_L \tag{31}$$

where the 'L' stands for 'linked'. The resolvent operator, $R_0 = (E_0 - H_0)^{-1}Q$, pre-supposes a separation of the Hamiltonian into $H=H_0 + V$, so that the full resolvent's, $R=(E-H)^{-1}Q = R_0 + R_0VR$, expansion (and re-organization of terms to correspond to a specific order) provides the traditional RSPT expansion.[12] But MBPT is much simpler. Unlike normal RSPT, *there are no renormalization terms in the linked form*. The reason is that all renormalization terms correspond to 'unlinked' diagrams so there are none allowed by the theorem. The energy is obtained from projection of the Schrödinger equation,

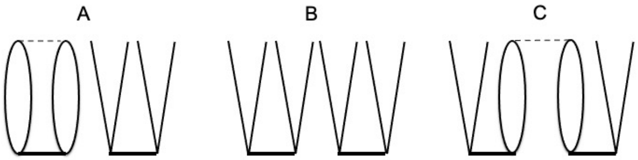


Fig. 2 Diagram A is unlinked since it has a 'closed' disconnected part. Any such closed part comes from the energy, and the LDT (Linked Diagram Theorem) eliminates all of them from the start. Diagram B is a 'linked' but 'disconnected' wavefunction contribution to the LDT, as the two parts are both open. Such terms arise from the LDT as in $\frac{1}{2}T_2^2$. Diagram C is a linked, connected contribution to a T_2 cluster amplitude. The T_2 amplitudes equations depend solely upon such connected terms.

$$E_{MBPT} = \langle 0|H|0\rangle + E^{(2)} + E^{(3)} + E^{(4)} + .. \quad (32)$$

$$E^{(k+1)} = \langle 0|H(R_0H)^k|0\rangle_L. \quad (33)$$

In the simplest case of a canonical HF reference function, $E_0 = \sum_{i=1}^{n} \varepsilon_i$,and $H_0 = \sum_{i=1}^{n} \widehat{f}(i)$,where the Fock operator, $\widehat{f}$,provides $H_0 = \sum f_{pp}\{p^\dagger p\} = \varepsilon_p\{p^\dagger p\}$. This special case of MBPT is sometimes called Moeller-Plesset PT, but that name hides its far more significant origin in the linked-diagram theorem of MBPT. To close the cycle, one sees that the LDT

$$\Psi_{MBPT} = |0\rangle + \sum_{k=1}^{\infty} (R_0H)^k|0\rangle_L = \exp(T)|0\rangle = \Psi_{CC} \quad (34)$$

$$E_{MBPT} = \langle 0|H|0\rangle + E^{(2)} + E^{(3)} + E^{(4)} + ... \quad (35)$$

$$E_{CC} = \langle 0|H\exp(T)|0\rangle = \langle 0|\exp(-T)H\exp(T)|0\rangle = \langle 0|\overline{H}|0\rangle \quad (36)$$

Hence, it should be apparent that CC theory provides an infinite-order summation of MBPT, and that both rest upon the LDT that greatly simplifies solutions of the Schrödinger equation. The interplay between infinite-order CC and finite order MBPT is integral to mny developments in CC applications like CCSD(T).[13]

Clearly, in the FCI there are no contributions from 'unlinked' diagrams or, equivalently, RSPT renomalization terms, all of which are of the form, $\Delta ES(\Psi)$, meaning an energy, represented by *closed diagrams* is multiplied by some function of the wavefunction's overlap, as in Figure 2A. The solutions to an eigenvalue equation for TCI inevitably has an energy dependence. Hence, *the retention of unlinked diagrams in TCI approximations is why they offer upper-bounds to the energy* and is why TCI approximations are not size-extensive, a damning failure of CI theory. The future of quantum chemistry demands the vastly improved approximations that emerge from the exponential wavefunction of CC theory, making the LDT the cornerstone of *the evolution to simplicity'* in quantum chemistry.

The distinction between 'connected' and 'linked' in Fig. 2 is that in CC theory all T operators are obtained from the commutator expansion in Eqn. (25), so the CC equations for the T amplitudes have to be connected. But the linked wavefunction of Eqn. 16 that is $\exp(T)|0\rangle$ includes both connected and disconnected terms, and both contribute to CC's connected, energy independent, algebraic equations. To the contrary, any TCI eigenvalue equation is E dependent, except for the FCI. The reason it is not is that $\Psi_{FCI} = \exp(T)|0\rangle$, without any limitation in T through T_n and since all CC equations are E independent and the FCI corresponds to the n-electron CC solution, its set of algebraic equations are independent of E. However, any TCI would be energy dependent, as RSPT renormalization terms and unlinked diagrams have to be retained until the FCI is reached.

Another interesting point regarding the H_2 lattice problem is that the four terms that arise from the non-linear term, $\frac{1}{2}T_2^2$, drawn and interpreted in Fig. 3, includes two terms, A and B, that can be identified as part of the CID wave function that must be there to enable the method to give the exact CID for two electrons, in the absence of single excitations.

The telltale feature that tells you A and B arise in CID is their dependence upon occupied orbitals[14] while the other two are new terms that arise in CCD. and do not have this feature. This is a place where only many-body diagrams provide this simplifying theorem. The first set of terms are called 'Hole-Conjoint' (HCJ) in our terminology. It means they have 'internal hole lines' that connect two T vertices, while all other terms do not and are thus, non-HCJ (NHCJ). This is a rigorous theorem. The first set guarantees the exact FCI result for n electrons. Thus, if one only includes A and B in CCSD then this defines 2CC, the exact solution for two electrons now including the singles. Without the singles, or with Brueckner orbitals, the same approximation has been called ACP-4,5 by Paldus[15], [16] and ACCD by Dykstra.[17] The point is that neither full CCD or CCSD is required to guarantee exact results for two electrons. 2CC does that with fewer terms and adds the effect of T_1 discussed below. And because only linked terms are included in the approximation, 2CC has to be extensive and exact for all non-interacting products of two electrons. It also rigorously defines *a size-extensive, (non-variational) CISD approx-*

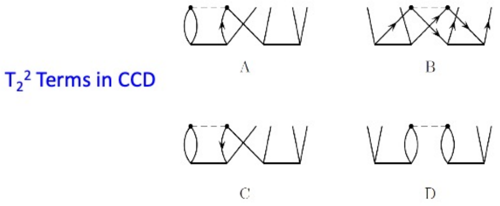


Fig. 3 The interpretation of these diagrams is $A = -\frac{1}{2}P(ij)\langle kl||cd\rangle t_{kl}^{cd} t_{lj}^{ab} = -\frac{1}{2}P(ij)\varepsilon_{li} t_{lj}^{ab}$; $B = \frac{1}{4}\langle kl||cd\rangle t_{ij}^{cd} t_{kl}^{ab}$; $C = -\frac{1}{2}P(ab)\langle kl||cd\rangle t_{lk}^{ac} t_{ij}^{db} = -\frac{1}{2}P(ab)\varepsilon^{da} t_{ij}^{db}$; $D = \frac{1}{2}\langle kl||cd\rangle t_{ik}^{ac} t_{jl}^{bd}$. All are summed over repeated indices.

imation that had often been a goal of prior work. Furthermore, 2CC is the only, correct, orbitally invariant CEPA[18,19] approximation.

Also, importantly, and unlike CID in this example, 2CC must separate correctly into non-interacting, closed-shell two-electron, H2 terms. These are the two sides of the extensivity coin: one pertains to scaling to NH2 units, while the reverse is the correct separation of the NH2 cluster into its non-interacting units.

As is well-known, for separation into open-shells, the reference function must also separate correctly, too. This is the reason one often chooses UHF based CC results for such problems.

The breakdown into HCJ and NHCJ allows one to retain only HCJ terms in CCSDT and CCSDTQ and still get the exact answer for 3 and 4 electrons, i.e., 3CC and 4CC. These are less computationally demanding than CCSDT and CCSDTQ, as the NHCJ terms that can be ignored come from non-linear CC terms. In particular, 3CC has been shown to do very well.[20,21]

The terms A and C have, unfortunately, sometimes been called ‘exclusion principle violating’ (EPV) diagrams that formally create a particle in ‘time’, (the fictitious vertical axis of the diagram), before another is deleted. But, of course, none of these terms violate the exclusion principle. Many-body approaches simply count terms differently. Unlike CI, where every determinant satisfies the Pauli principle, many-body methods allow for the inclusion of determinants that are exactly zero since they contain two identical orbitals, e.g., leading to the linked diagram structure. This is why all CC/MBPT expressions written in terms of integrals are conveniently represented in unrestricted particle and hole summations, unlike restricted sums like$\sum_{ia \neq jb}$ that can occur in CI. This fact and its enormous computational simplification has not always been fully appreciated, but are fundamental to many-body theory and the 'Evolution Toward Simplicity."

B.The Evolution Toward Simplicity

(I) The first step is the Linked Diagram Theorem. This eliminates all unlinked diagrams that would still be in a TCI, even though they would not be in the FCI. Their removal guarantees better wavefunction approximations that depend upon higher excitation terms that arise from the CC non-linear equations.

(II) The second step is the elimination of disconnected terms in the CC amplitudes via the BCH theorem. This provides the essential subset of amplitudes required in the FCI wavefunction with no redundancy.

(III) The third simplification is that all approximations for CC (and MBPT) will be size-extensive, meaning the correct wavefunction and energy for one unit is also the correct wavefunction and energy for N non-interacting units.

(IV) As a consequence, the correct wavefunction for an infinite system like a polymer or a crystal is extensive, providing meaningful correlated results unlike those from TCI whose correlation part has zero overlap with the exact wavefunction.

This follows because the exact solution for the infinite system has to scale linearly with N. But any TCI has to scale as N^2 or higher because of its unlinked diagrams. Thus, the overlap for the exact correlated solution compared to the TCI is zero.

C. Role of single excitations, T_1.

Adding single excitations T_1 to T_2 , $[T_1, T_2] = 0$, defines $\Psi_{CCSD} = \exp(T_1)\exp(T_2)|0\rangle$ causing the CCSD equations to be of the form,

$$Q_1 D_1 T_1|0\rangle = Q_1[f + WT_1 + (f+W)T_2 + (f+W)T_1T_2 + (f+W)T_1^2/2 + WT_1^3/3!|0\rangle_C \tag{37}$$

$$Q_2 D_2 T_2|0\rangle = Q_2[W + WT_2 + (f+W)T_2^2/2 + WT_1 + WT_1^2/2 + (f+W)T_1^3/3! + WT_1^4/4! + (f+W)T_1T_2 + (f+W)T_1^2T_2/2|0\rangle_C \tag{38}$$

The above shows the general structure of the CC equations for the connected amplitudes, T_1 and T_2.[22] Note, there is a potential contribution from the f operator as well as the two-electron, W, operator. The diagonal part of the f operator in $H_0 = \sum_p f_{pp}$ has already been taken to the left side of the equation, so that $Q_1 D_1 T_1|0\rangle = D_i^a t_i^a$ means $(f_{ii} - f_{aa})t_i^a$ and $Q_2 D_2 T_2|0\rangle = (f_{ii} + f_{jj} - f_{aa} - f_{bb})t_{ij}^{ab\cdot}$. All other contributions are from off-diagonal f_{pq}. The antisymmetrized Goldstone diagrams we always use[11] provide routine, unambiguous generation and uniquely translate these general equations into precisely what they are in their algebraically connected form, with line directions, all factors of two, and their sign, and without redundancy! But these kind of details are left to other sources[11] in our attempt to convey what really matters in CC theory without diagrammatic distractions.

CCSD has two prominent new features: (1) CCSD provides the correct density through first order in MBPT, and along with the initial contribution of T_2, all second-order terms. (2) CCSD, 2CC, and higher calculations benefit from the theorem that $\exp(T_1)|0\rangle = |\Phi\rangle$, meaning a new, orbital rotated determinant. So any set of orbitals that constitutes the $|0\rangle$ determinant can be rotated to a new set of orbitals that defines a new determinant, $|\Phi\rangle$. So in a sense, CCSD generates the orbitals it wants during the calculation. (They can be extracted from the T_1 amplitudes after the calculation if of interest.) This makes it and higher variants like CCSDT, CCSDTQ, etc. 'insensitive' to orbital choice, reaching complete orbital invariance at the FCI limit. This orbital insensitivity pertains to mixing occupied orbitals and virtual ones. Of course, it is also true that any normal CC wavefunction CCSD, CCSDT, ... will be invariant to mixing just occ-occ or virt-virt, but the additional insensitivity of CCSD arises from its built-in occupied-virtual rotations. CISD, e.g., will have occ-occ and virt-virt invariance, but will be quite sensitive to occ-virt mixing making the choice of orbitals far more important as in MCSCF, e.g.

To illustrate this insensitivity, consider an example from long ago.[23] The objective is to do CCSD for a DZP basis set starting from a 'back-of-envelope' set of local minimum basis 'bond-orbitals' for methane. The non-variational occupied orbitals are composed of sp3 hybrids $C(sp^3)+H(1s)$, while the principal 'anti-bonding' ones are $C(sp^3)$-$H(1s)$. From this reference, low-order perturbation theory is used to get the energy. Hence, the term, 'perturbed CI with localized orbitals' (PCILO).[24] Using its bond-orbitals to define a minimum basis (MBS), non-variational approximation, while the rest of the basis set consists of the full DZP basis minus the MBS and all functions are orthogonalized; this MBS variational expectation value gives an energy of -40.080 au compared to its DZP variational SCF value of -40.200 au, a 117.55 kcal/mol difference. But, even starting from the MBS approximation, the correlated CCSD calculation exploits $\exp(T_1)$ to bring in the other basis set terms to converge quickly to a numerical correlated result of -40.3732, a difference at convergence compared to the DZP basis SCF-CCSD of only -0.66 kcal/mol. This is the power of $\exp(T_1)$!

V. The fifth step in our evolution toward simplicity is flexibility of orbital choice in correlated calculations.

Including $\exp(T_1)$ in CC wavefunctions makes most orbital choices in calculations relatively unimportant, and even less so, once T_3 and higher clusters are added, rapidly converging to the complete orbital invariance of the FCI.

This numerical flexibility is not to say that choice of orbitals has no interpretative value in quantum chemistry.[25] Ruedenberg proposes such sets of MCSCF or (FORS) orbitals and uses them for interpretative value.

In fact, the idea of a 'correlated orbital theory'[26] that is derived from CC/EOM theory is meant to provide a set of *correlated ab initio* orbitals that can, arguably, best describe chemistry, conceptually and numerically.

One caveat to the numerical orbital insensitivity in V. is when a reference determinant is qualitatively different like broken symmetry UHF solutions used in bond breaking or lies outside the domain of the $\exp(T_1)$ rotation. Then some calculations might call for a different single determinant function. At the FCI limit, however, even that would not matter. Some might think that Kohn-Sham choices might be an improvement because the virtual orbitals and occupied ones share the same potential, unlike Hartree-Fock electrons where those in virtual orbitals feel a V^n potential while those in occupied orbitals see a V^{n-1} one. But not in practice in CCSD and beyond since they span the same space and all of it is used in a CCSD calculation at that level. If for some reason the MO space is limited to a subset of virtual orbitals, then there could be important numerical differences between HF and KS CC, and other choices, particularly, for finite MBPT, where the infinite-order effect of T_1 might not be fully achieved.

This is a failing of the so-called QCISD and QCISD(T) methods[27] where the CCSD $\exp(T_1)$ exponential dependence on T1 is truncated. The latter causes the dramatic three-orders of magnitude[28] error in the IR-intensity of BeO compared to CCSD and CCSD(T). 2CC like CCSD avoids any such pathological behavior because all effects of $\exp(T_1)$ are included, even though only two of the four terms in the quadratic correction are required.

Another common failing of HF is the so-called 'HF pathology', meaning that for metal systems, HF provides a band-gap (due to the V^n and V^{n-1} potential mentioned above), while KS would not, so a KS reference might be expected to help for metal containing molecules. But so far, there is little evidence that this matters even in the recent near-metal CCSD and EOM-CCSD calculations done for solids.[29] Remember, it is well-known that ground state RPA is applicable to metals, and it is an approximation to CCD that consists of the sum of just ring diagrams. The key is that it is infinite-order as are CC approximations. Finite MBPT will obviously fail for metals without further generalization that eliminate any dependence on a band-gap, but infinite-order sums can be built into MBPT, too, in other ways than CC.[30]

Related to this orbital insensitivity is the profitable use of what we call, 'quasi-restricted HF', (QRHF) orbitals.[31] In many applications the choice of orbitals from a variational HF source provides it own pathologies. A good example is something as simple as using coupled-perturbed HF (CPHF) to build in HF orbital relaxation subject to a perturbation like an electric or magnetic field. In many cases the CPHF (or equivalently TDHF) equations turn out to be singular for the perturbation giving a negative excitation energy in TDHF and the lack of variational stability for the HF approximation. This makes using the CPHF relaxed orbital choice unusable for CI, e.g. The solution in CCSD is to bypass the variational, relaxed HF solution by simply using the orbitals in their unrelaxed form to define a QRHF determinant and allow CCSD to put in the correct, orbital relaxed, correlation corrections as part of its calculation without the intermediate step;[32] something that CI cannot do. Some easily generated QRHF choices would be orbitals from cations or anions to treat a neutral molecule or vice versa or orbitals from an adjacent point on a PES.

Another recent example of flexible orbital choice is offered by the singularities encountered between the five unit arene and six unit one.[33] As shown in Fig. 4, the variational RHF solution interchanges the occupied orbitals for the reference single determinant and that affects the subsequent CCSD solution causing it not to converge for the five-mer, while on either side of the five-unit oligomer there is no convergence difficulty for the CCSD calculation starting from the RHF reference. But using the QRHF strategy one can pick a set of orbitals that does not have this variational artifact to provide a way to fix this discontinuity. If the discontinuity is 'real' it should show up at the CCSD or a higher level. Otherwise, it is an artifact of the independent particle model that defines the reference determinant.

The solution here is to switch to a KS-DFT solution (PBE in this case[34]) that does not show the orbital interchange, then allow CCSD to use its power to 'fix' the non-variational orbitals as part of the calculation to yield a correct CCSD result as Fig. 4 shows. The CCSD energy difference between the RHF reference when viable and PBE is virtually zero, but the artifactual discontinuities are removed to provide a smooth dependence upon oligomer size.

Another interesting example is to use what we call 'template' orbitals[35]. That is we take a set of orbitals for some suitably chosen system like a particular transition metal atom multiplet and occupy them in various ways to describe the possible atomic multiplets. Many would say such problems should be done with MR methods because of the near degeneracy of the orbitals and the multiplet energies, but the insensitivity of CCSD and beyond to orbital choice allows such calculations to reliably sort out the closely lying multiplet energies based upon one set per atom of template orbitals, usually generated by using fractional occupation numbers to provide a set of five degenerate orbitals that can be occupied to define any multiplet. In fact, having the same set of orbitals facilitates obtaining accurate energy differences among multiplets.

The flexibility of CCSD and its higher cluster analogs to use any convenient set of orbitals opens the door to many correlated applications that would be impossible in an orbital dependent theory like CI, while moving closer to the ultimate FCI's orbital invariance.

In our work we routinely use natural, Brueckner, KS, QRHF, template, and other choices of orbitals depending upon the objectives of the calculation, but because of CCSD and higher approximations' orbital insensitivity, except in a few cases, there will be little difference in the energy or density matrix[4] because of the role of T1. This also pertains to orbital optimized CC that might show some potentially improved results at the CCD level[36] but seldom at the CCSD one. Of course, once normal CCD is truncated in some manner as in 'pair restricted CCD' (pCCD) discussed later, there is no more orbital invariance and orbital optimization is hoped to allow the truncated pCCD approximation to be better. But note, such approximations are not extensive.

Before finishing with orbital choice, it should be noted that the use of Frozen Natural Orbitals, FNOs, meaning the virtual orbitals normally taken from a MBPT2 response density matrix, subject to keeping the occupied orbitals fixed[37] provides an orbital occupation number that enables a truncation of up to ≈40% of the virtual space to use in subsequent CCSDTQ... calculations.[38] The results for the CC energy, subject to using the MBPT2 energy in the untruncated basis and then doing CCSDTQ... for the increment show very little loss in accuracy. This enables one to obtain high-order CC results at effectively the basis set limit of the MBPT2 calculation, but now truncated to fixed computational levels like DZP, TZP, etc. to make the higher-order CC calculations doable.[39]

The other orbital choice that has been shown to pay great dividends in CC is the use of 'pair natural orbitals' PNO, as developed by Neese and collaborators[40]. Unlike FNO's, the non-orthogonal PNO's are not simply a natural orbital rotation but have to be explicitly built into CC programs. But such orbitals enable the realization of the linear scaling property that is implicit in size-extensive CC methods as discussed at the start of this perspective, but still require a computational strategy that achieves numerical linear scaling.

Some alternative 'domain specific' attempts at achieving numerical linear scaling in CC have also been pursued[41,42].

D. Density matrices and properties in CCSD.

The general treatment of properties in CCSD required new theory, because previous work applied to variational wavefunctions offered simplifications that do not apply for CC ones, where nothing is variational: not the amplitudes, the orbitals, or the Gaussian atomic basis set. Furthermore, even the concept of an expectation value

$$\begin{aligned}\langle\widehat{O}\rangle &= \frac{\langle 0|\exp(T^{\dagger})\widehat{O}\exp(T)|0\rangle}{\langle 0|\exp(T^{\dagger})\exp(T)|0\rangle} \\ &= \langle 0|(\exp(T^{\dagger})\widehat{O}\exp(T))_C|0\rangle\end{aligned} \tag{39}$$

though formally correct in the limit does not terminate,[11] causing it not to be defined in the traditional way when T is truncated. If $\widehat{O}$ is chosen to be the Hamiltonian, a little algebra and use of the resolution of the identity shows that

$$\langle\widehat{H}\rangle = \frac{\langle 0|\exp(T^{\dagger})\exp(T)\exp(-T)\widehat{H}\exp(T)|0\rangle}{\langle 0|\exp(T^{\dagger})\exp(T)|0\rangle} \tag{40}$$

$$= \frac{\langle 0|\exp(T^{\dagger})\exp(T)(P+Q)\exp(-T)\widehat{H}\exp(T)|0\rangle}{\langle 0|\exp(T^{\dagger})\exp(T)|0\rangle} \tag{41}$$

$$= \langle 0|\overline{H}|0\rangle \tag{42}$$

When using the CC amplitude solutions for *all possible Q space excitations* in the FCI,

$$0 = Q\overline{H}|0\rangle \tag{43}$$

and eliminating the denominator from P=$|0\rangle\langle 0|$,

$$E_{CC} = \langle 0|\overline{H}|0\rangle \tag{44}$$

So the equivalence between the expectation value and the closed form energy is apparent in the untruncated case, but one wants a general, closed-form for any property at useful truncations like CCSD.

To define properties other than the energy, consider the derivatives of E_{CC}. In the usual development all properties can be obtained by adding a perturbation of some sort to the $\widehat{H}$, that is $\widehat{H}(\lambda) = \widehat{H} + \lambda\widehat{O}$, and using the Hellman-Feynman theorem,

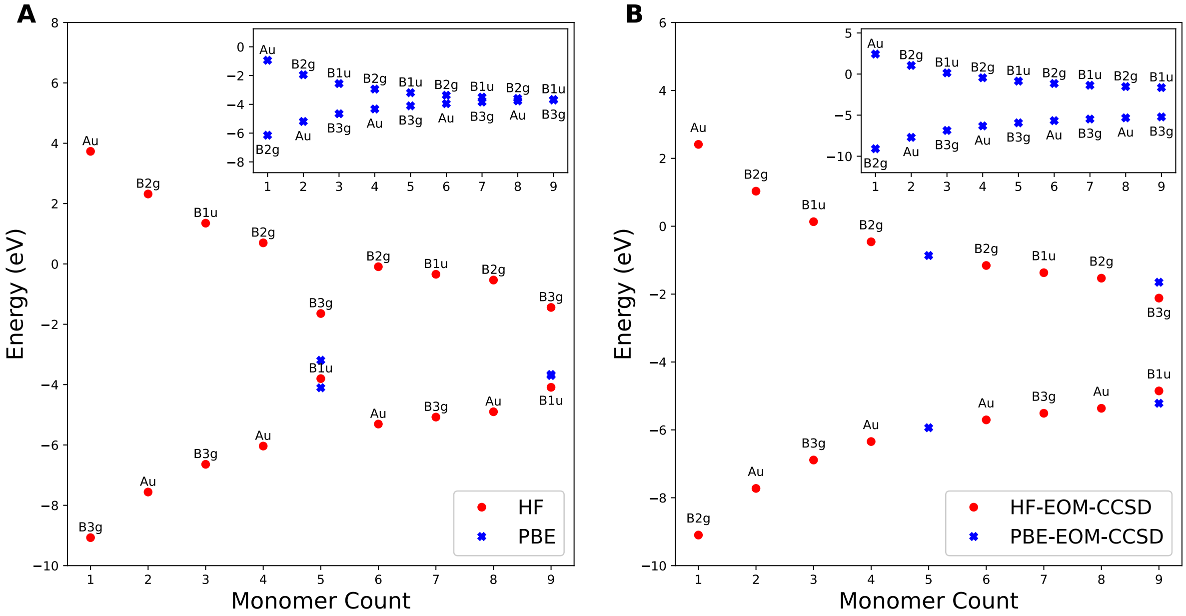


Fig. 4 A) depicts the inherent discontinuity at the 5mer and 9mer as predicted by HF and that from the PBE KS-DFT functional. B) Illustration of the CCSD results subject to the different reference functions.choices. Notably, all discontinuities are resolved.

$$\partial \widehat{H}(\lambda)/\partial \lambda = \langle \Psi|\widehat{O}|\Psi\rangle + \tag{45}$$

$$\langle \frac{\partial \Psi}{\partial \lambda}|\widehat{H}-E|\Psi\rangle + \langle \Psi|\widehat{H}-E|\frac{\partial \Psi}{\partial \lambda}\rangle \tag{46}$$

$$\frac{\partial E}{\partial \lambda}\langle \Psi|\Psi\rangle = \langle \Psi|\widehat{O}|\Psi\rangle \tag{47}$$

to obtain the expectation value. But this derivation assumes that

$$\langle \frac{\partial \Psi}{\partial \lambda}|\widehat{H}-E|\Psi\rangle + \langle \Psi|\widehat{H}-E|\frac{\partial \Psi}{\partial \lambda}\rangle = 0 \tag{48}$$

as if $\widehat{H}\Psi = E\Psi$. But this is not necessarily true for approximate wavefunctions. In a calculation there are three components in Ψ : the atomic orbital basis set and its location, χ, the MO basis, $\varphi = \chi\mathbf{c}$, and the CI coefficients, $\Psi = \mathbf{hC}$, relative to the determinantal basis set. Then the variation, $\delta\Psi$, gives

$$\delta\Psi = (\partial\Psi/\partial\chi)\delta\chi + (\partial\Psi/\partial\mathbf{c})\delta\mathbf{c} + (\partial\Psi/\partial\mathbf{C})\delta\mathbf{C} \tag{49}$$

When the energy is used to variationally determine Ψ, $\delta E = \langle\delta\Psi|H|\Psi\rangle + \langle\Psi|H|\delta\Psi\rangle = 0$, the three components above need to be considered.

$$\delta E = (\partial E/\partial\chi)\delta\chi + (\partial E/\partial\mathbf{c})\delta\mathbf{c} + (\partial E/\partial\mathbf{C})\delta\mathbf{C} \tag{50}$$

The advantage of the variational principle in CI is the last term vanishes. In MCSCF, the last two terms would vanish. But the location of the χ functions is not optimum and must be retained for any wavefunction using Gaussian orbitals located on atoms. Note, even in a normal CI the MO dependent terms do not vanish but would contribute to the result. So the simple CI expectation value for a property does not satisfy such a simple Hellman-Feynman theorem.

To develop the CC theory for properties, consider the second-quantized Hamiltonian from Eqn. 26 and its derivative, $\partial H/\partial X_\alpha$. For analytical gradients, X_α, would be one of the 3N atomic degrees of freedom for a molecule, while an electric field property would add to this Hamiltonian an external perturbation like $\sum_p \varepsilon\cdot\mathbf{r}_p$,and obtain properties from the components of $\partial H/\partial\varepsilon$ for the dipole moment. Second derivatives would provide the Hessian and the dipole polarizability, etc.

$$H = \sum_{p,q} f_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{p^\dagger q^\dagger sr\} + \langle H\rangle \tag{51}$$

$$\partial H/\partial X_\alpha = \sum_{p,q} f^\alpha_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle^\alpha\{p^\dagger q^\dagger sr\} \tag{52}$$

The second quantized version of these operators already takes care of a lot of information in a compact form.

$$\langle p|\widehat{f}|q\rangle^\alpha = \langle p|\widehat{h}+\widehat{J}-\widehat{K}|q\rangle^\alpha \tag{53}$$

$$= \langle p|h^\alpha + J^\alpha - K^\alpha|q\rangle + \langle p^\alpha|f|q\rangle + \langle p|f|q^\alpha\rangle \tag{54}$$

Notably,

$$q^\alpha = \sum_\mu \chi^\alpha_\mu c_q + \sum_\mu \chi_\mu c^\alpha_q \tag{55}$$

and inserting this into f^α_{pq} and $\langle pq||rs\rangle^\alpha$ provides the detailed expression[43] that in addition to $h^\alpha = \partial H/\partial X_\alpha$, —the simple Hellman-Feynman term—gives a term from the AO basis functions evaluated by integral derivatives, and a second term due to the derivatives of the MO coefficients evaluated by CPHF theory when using a HF reference, or its equivalent for other reference determinants. The third quantity required is the derivative T^α that arises from differentiation of the E_{CC} expression, Eqn. 38.

$$\langle 0|\partial E_{CC}/\partial X_{\alpha}|0\rangle = \langle 0|\overline{H}^{\alpha}|0\rangle + \langle 0|\overline{H}T^{\alpha}|0\rangle \tag{56}$$

The derivative is separated into two parts, a part that depends upon $\overline{H}^{\alpha}$ after separating out the contribution from T into T^{α}. To actually use this as written would require the computation of $\sim$3N T^{α} quantities, obviously a hopeless proposition. Instead, one considers the derivative of the CC equations themselves,

$$QT^{\alpha}P = Q(E_{CC} - \overline{H})^{-1}Q\overline{H}^{\alpha}P = RQ\overline{H}^{\alpha}P \tag{57}$$

which then provides the expression,

$$E^{\alpha}P = P\overline{H}^{\alpha}P + P\overline{H}QRQ\overline{H}^{\alpha}P \tag{58}$$

Notice the introduction of the resolvent operator as $QT^{\alpha}P$ corresponds to the first-order perturbed wavefunction, $QT^{\alpha}P = QRQ\overline{H}^{\alpha}$.

The $\alpha-$derivative independent quantity

$$\Lambda = P\overline{H}QRQ \tag{59}$$

provides a set of Λ de-excitation equations that incorporate the resolvent operator such that no inverse matrices are directly involved. With Λ, the Generalized Hellman-Feynman expression for the derivative is

$$E^{\alpha}P = P(1+\Lambda)\overline{H}^{\alpha}P \tag{60}$$

Its integral is the CC functional,

$$EP = P(1+\Lambda)\overline{H}P \tag{61}$$

that provides the derivative immediately once one observes it is stationary wrt to Λ and T,

$$\delta E/\delta\Lambda = Q\overline{H}P = 0 \tag{62}$$

$$\delta E/\delta T = P(1+\Lambda)\overline{H}Q = 0 \tag{63}$$

The *linear* Λ equations above, presented in detail elsewhere,[11] are decoupled from T but must be obtained along with T in a typical CC calculation. So henceforth, an expectation value in CC theory for some operator $\widehat{O}$ is

$$\langle 0|\widehat{O}|0\rangle = \langle 0|(1+\Lambda)\exp(-T)\widehat{O}\exp(T)|0\rangle \tag{64}$$

This is obviously a 'response' derivation as it derives from an energy derivative. In particular, it provides the one-particle 'response' density matrix,

$$\gamma_{qp} = \langle 0|(1+\Lambda)\exp(-T)\widehat{p}^{\dagger}\widehat{q}\exp(T)|0\rangle \tag{65}$$

In the particular case of analytical gradients, the MO relaxation effect has to be present to provide a well-defined critical point on a PES. That is handled by adding to the response density matrix orbital relaxation into a "relaxed" variant, D_{pq},[43] into a new density matrix. So there are two choices for other properties than gradients: orbital relaxed or not. The numerical differences are usually small because of CCSD's insensitivity to orbital choice discussed above. Furthermore, even the small numerical effects of the orbital relaxation can be shown to be naturally incorporated into the response density matrix obtained subject to the unrelaxed orbitals once triple excitations are added,[44] like in the CCSDT-n methods discussed below.[45,46]

Notice, in these derivations there is no neglect of the non-Hellman-Feynman terms. Consequently, CC expectation values are more complete than typical expectation values evaluated in CI where it is assumed that its variational property eliminates the non-Hellman-Feynman terms. In methods like CI, the variationally determined CI amplitudes simplify the equations compared to CC theory, but TCI is not fully variational for the MO's unless a MCSCF is done, and thus, retains non-Hellman-Feynman terms. As long as all methods use AO basis sets attached to atoms, nothing is variational about the AO dependence unless floated off their atomic centers to an optimum location for each Gaussian function.[47] Plane-wave bases that have no dependence on atomic centers are used for crystals and polymers and occasionally for molecules do not have this issue, but have other issues like correctly describing inner shell electrons. The latter usually requires psuedo-potentials.

VI. For analytical gradients and first-order properties, the 'Evolution toward Simplicity' demands that approximate quantum chemical expressions satisfy an appropriate form of a generalized Hellman-Feynman theorem as derived above from response theory.

The one-particle, response density matrix itself in Eqn. 65 describes all other first order properties and is used to generate the CC natural orbitals. There are many uses for the natural orbitals in application. One we have studied is to use the natural orbitals to define a set of indices to identify residual multi-reference character in single reference (SR) CC calculations[4]. As this is often thought to be the remaining error in a SR-CC calculation once the basis set and level of correlation are good, it is nice to be able to quantify this effect along with the others in a calculation.

We do this by appealing to the fiction of a wavefunction that can be represented as a single determinant of just n (number of electrons) occupied, correlated, spin-orbitals. This determinant, unlike the first natural determinant, is meant to retain no additional contribution from the unoccupied orbitals in the basis set. Hence, it is a virtually exact set of correlated orbitals somewhat like natural or Brueckner but also like Kohn-Sham, where only n are required. Using this device, MR character is identified by how important the M-n virtual natural orbital occupation numbers are that remain in the response density matrix of SR-CC. We call that value the external electron number (EEN), and use it and its variants, to define four different multi-reference indices that are shown to correctly identify MR character in molecules undergoing bond-breaking. This work also shows that the indices generated normally fall well below the threshold of MR character once a UHF reference determinant is used instead of an incorrectly separating RHF one.

E. Role of connected triple excitations, T_3.

Since CCD already includes all T_2^2 terms, it benefits from all fourth-order energy CI quadruples, and implicitly from sixth-order contributions from hextuples. This makes the contribution of connected triple excitations, T_3, the most important term not yet included after T_2 and T_1. This is very different than CI where C_4 is more important than C_3.The figure in Ref.[1] shows CI, MBPT, and CC at different levels plotted against FCI makes this abundantly clear, as does Fig. 5.

For higher cluster operators like T3 and T4, further perturbation corrections from MBPT will be very important. The connection between CC and MBPT starts with a separation of the normal ordered Hamiltonian,

$$H = H_0 + V \tag{66}$$

$$H_0 = \sum_{ij} f_{ij}\{i^\dagger j\} + \sum_{ab} f_{ab}\{a^\dagger b\} \tag{67}$$

$$V = \sum_{ia} f_{ia}\{i^\dagger a + a^\dagger i\} + W \tag{68}$$

The occupied-virtual part, $f_{ia} = f_{ov}$, is now added to the two-particle operator, W, to define the perturbation. Since the CC equations are invariant to occ-occ and virt-virt rotations, one can use that freedom to rotate the orbitals to a semi-canonical form, where for the rotated orbitals, $f'_{ij} = f_{ii}\delta_{ij}$ and $f'_{ab} = f_{aa}\delta_{ab}$,while f'_{ia} remains as part of the perturbation with W'. A special case of semi-canonical orbitals are the canonical HF orbitals where $f_{ii} = \varepsilon_i$ and $f_{aa} = \varepsilon_a$, and $f_{ia} = 0$. But we want to have the flexibility to use any orbitals in CC calculations like ROHF, natural, Brueckner, GVB, KS, Orbital-Optimized, QRHF, template, etc. and for these $f_{ia} \neq 0$.Henceforth, we will assume the semi-canonical orbitals as a transformation of any non HF set, but suppress the ' in the expressions, so $H_0 = \sum f_{pp}\{p^\dagger p\}$.

To introduce triple excitations into CC theory, we consider the wavefunction, $\Psi_{CCSDT} = \exp(T_1)\exp(T_2)\exp(T_3)$. Following the usual procedure of projecting this wavefunction onto all single, double, and triple excitations, one gets a coupled-set of non-linear equations,

$$0 = \langle\Phi_i^a|[H\exp(T)]_C|0\rangle \tag{69}$$

$$0 = \langle\Phi_{ij}^{ab}|[H\exp(T)]_C|0\rangle \tag{70}$$

$$0 = \langle\Phi_{ijk}^{abc}|[H\exp(T)]_C|0\rangle \tag{71}$$

that define CCSDT, $T_4, T_5 = 0$.The correlation energy derives solely from single and double excitations having the form,

$$E_{CC} = \langle 0|[HT_2 + HT_1 + HT_1^2/2]|0\rangle_C \tag{72}$$

$$= \langle 0|[WT_2 + fT_1 + WT_1^2/2]|0\rangle_C \tag{73}$$

$$E_{CC} = \frac{1}{4}\langle ij||ab\rangle(t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) + f_{ia}t_i^a \tag{74}$$

the latter summed over repeated indices. Hence, all triples effects would be introduced from the contribution of T_3 into T_2 and T_1 and subsequently to the energy. Thus, the CCSDT equations can be written in the informative way,

$$Q_3D_3T_3|0\rangle = Q_3[H\exp(T_1+T_2)]_C + [H\exp(T_3)]_C$$
$$+ [HT_3\exp(T_1+T_2)]_C \tag{75}$$

$$= Q_3[\widetilde{H} + ([HT_3 + \widetilde{H}T_3]_C \tag{76}$$

where we have a separation of contributions from $\widetilde{H}$, then from linear T_3 alone, and finally from the cross terms, where the underlying CCSD uses the notation, $\widetilde{H} = [H\exp(T_1+T_2)]_{C.}$ Then,

$$Q_3D_3T_3|0\rangle = Q_3[WT_2 + WT_1T_2 + WT_2^2/2 + fT_2^2/2 + WT_3 + (\widetilde{H}T_3)]|0\rangle_C \tag{77}$$

Closer inspection of Eqn. 71 shows that WT_3 introduces an $\sim n^3N^5$ computational step that is excessive on top of CCSD's $\sim n^2N^4$ dependence and would require storing T_3 with its large, $\sim n^3N^3$, number of terms to evaluate it. But this term is a third-order contribution to the wavefunction, as are all the others shown except WT_2 that is second-order. Thus, to obtain the lowest-order terms in MBPT one takes this term to define the $T_3^{[2]}$ value

$$Q_3D_3T_3^{[2]}|0\rangle = Q_3(WT_2)_C|0\rangle \tag{78}$$

and insert it into the T_2 and the T_1 equation ,

$$Q_2D_2T_2^{[3]}|0\rangle = Q_2[WT_3^{[2]} + fT_3^{[2]}]|0\rangle_C \tag{79}$$

$$Q_1D_1T_1^{[3]}|0\rangle = Q_1[WT_3^{[2]}]|0\rangle_C \tag{80}$$

to provide the fourth-order triples MBPT energy,

$$E_T^{[4]} = \langle 0|WQ_2(WT_3^{[2]})_C|0\rangle + \langle 0|WQ_2(fT_3^{[2]})_C|0\rangle + \langle 0|fQ_1(WT_3^{[2]})_C|0\rangle \tag{81}$$

All other terms are higher than fourth-order. The first term with HF orbitals is now called [T][49]. It is the only fourth-order correction for HF. Adding the second term that is due to single excitations which is fifth-order in HF defines (T)[50]. All three terms are required for any choice of orbitals and single determinant reference function. They then constitute all non-HF fourth-order terms[51] in this orbital invariant form and by using semi-canonical orbitals, remains perturbative. This is the generalized form for (T).

Either we can leave all expressions in terms of some $QWT|0\rangle$ or $QfT|0\rangle$ form where the Q_nWT or Q_nfT dictates which particular W or f is needed at each stage, or we can start to distinguish among them by specifying which of the W's are used here and later in this perspective. There are 9 different W possibilities separated into five terms by how many creation-annihilation terms are involved. They are W= $W_{-2,}W_{-1,}W_{0,}W_{1,}W_2$. W_{-2} means reduce particle-hole number by 2, while W_2 would increase it by 2, and the others are indicated by their subscript, from 0 where no change occurs, or increasing by 1, W_1, or decreasing by 1, W_{-1}. This would tell us that the first term would be $\langle 0|W_{-2}Q_2(W_{-1}T_3^{[2]})_C|0\rangle = \langle 0|W_{-2}Q_2(W_{-1})(Q_3W_1T_2/D_3)|0\rangle_C$, e.g.

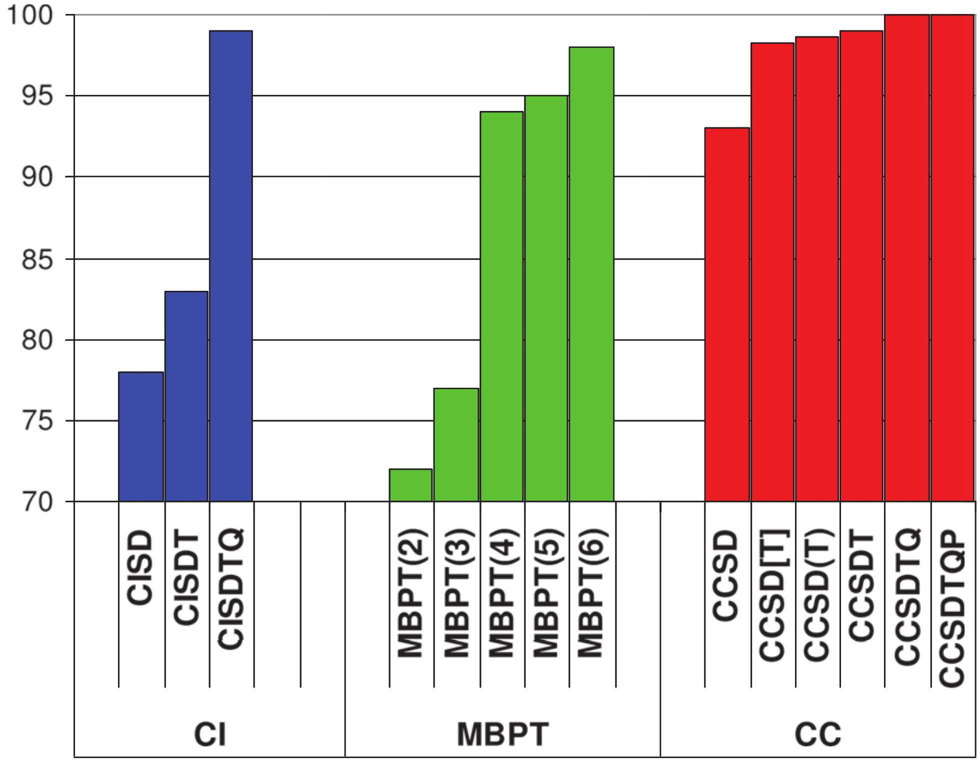


Fig. 5 Comparison of CI, MBPT, and CC results with full CI. Results averaged over the series of small molecules: BH, HF, H_2O, SiH_2 and CH_2 in DZP basis set at R_e, 1.5 R_e, 2.0 $_e$ and N_2 in cc-pVDZ basis set at R_e and C_2 in cc-pVDZ basis set augmented by diffuse functions at R_e.[48]

This step, of course, takes us closer to the explicit diagrammatic computational formulae. Similarly, f consists of 3 terms, $f_{-1,}f_{1,}f_0$. For this perspective, it should be easier to grasp this approximation in the algebraic form above than getting bogged down with all the diagrammatic details shown elsewhere[11] that provide explicit computational formulae.

The reason for the $^{[4]}$ notation is that the order designation can include converged infinite-order values from CCSD for $\overline{T}_2$ and $\overline{T}_1$ in some expressions like $\overline{T}_2$ in Eqn. 78, above, but once inserted into the expression are counted as generalized first-order terms. The pure first-order terms require that $T_2^{(1)} = W_{+2}/D_2$ and $T_1^{(1)} = f_{+1}/D_1$ and if those are used to evaluate $T_3^{(2)}$, the order would be pure second-order and $E_T^{(4)}$would then be the pure triples part of MBPT(4). Some early applications simply added $E_T^{(4)}$to the CCSD energy to provide better results as in the HF case only the first term survives in fourth-order, since $f_1 = f_{ov} = 0$.

But the best way to define the non-iterative (T) part of CCSD is to start from the viewpoint of the CC generalized expectation value or functional,

$$E_{CC} = \langle 0|(1+\Lambda)\overline{H}|0\rangle_C \tag{82}$$

and isolate just the triples part of this from T_3 and Λ_3,

$$\begin{aligned}E_T^{[4]} =& \langle 0|\Lambda_3 Q_3[H_0 T_3^{[2]} + (W_{+1}T_2)_C] + \Lambda_2 Q_2[(W_{-1}+f_{-1})T_3^{[2]})_C \\ &+ \Lambda_1 Q_1 (W_{-2}T_3^{[2]})_C|0\rangle \\ =& \Lambda_2 Q_2[(W_{-1}+f_{-1})T_3^{[2]})_C + \Lambda_1 Q_1 (W_{-2}T_3^{[2]})_C|0\rangle\end{aligned} \tag{83}$$

since the *Lambda*$_3$ terms on the right of Eqn. 83 disappear by virtue of Eqn. 71.. Given a converged $\overline{\Lambda}_1$ and $\overline{\Lambda}_2$ along with $\overline{T}_1$ and $\overline{T}_2$ from a prior CCSD calculation, Eqn. 83 provides a (T) to define ΛCCSD(T) (also called CCSD(T)$_\Lambda$ originally[52]. This is obviously correct through the fourth-order energy and second-order wavefunction. It also has the same orbital invariance properties as an iterative method like CCSDT or CCSDT-3, important to semi-canonical transformations, analytical gradients, and convergence to full CI comparisons, e.g. For HF orbitals the $Q_2 f_{-1} T_3^{[2]}$ term vanishes.

To a first approximation, $\Lambda \simeq T^\dagger$. Using $T^\dagger$ in place of Λ provides the expedient and widely used CCSD(T) approximation[50], but now generalized to non-HF, semi-canonical orbitals, and it has well-known perturbation theory shortcomings that ΛCCSD(T) can remove to a large degree as shown in Fig. 6.

In addition to this non-iterative approximation, one can define iterative $\sim$m^7 ones short of CCSDT that all start by eliminating the $T_{3-}$to $T_3 \sim$m^8 term. The most complete of these is to allow all possible T_1 and T_2 terms in $\widetilde{H}$ to contribute to T_3 and

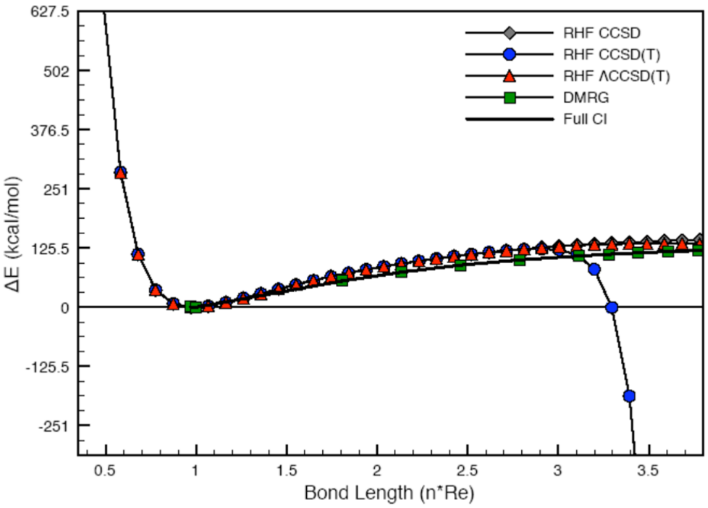


Fig. 6 Illustration of the limitations of perturbative corrections in CCSD(T) vs, ΛCCSD(T) for F2.[53]

T_3, in turn, to update T_1 and T_2 until the set of coupled equations converges. This is termed, CCSDT-3,[45] and should be the most orbitally insensitive approximation short of CCSDT[45]. Its predecessor, CCSDT-1[54], limited the $\widetilde{H}$ contribution to T_3 to just the lowest-order T2 terms. Both are correct through the fourth-order MBPT energy and second-order wavefunction. Any iterative method even with such approximations will perform much better than perturbative, non-iterative ones in difficult situations as in the RHF based bond breaking problems that cause the perturbative CCSD(T) to fail dramatically. But they do not always do as well as expected. Even CCSDT will typically overshoot the dissociation energy for a molecule when FCI results are available for comparison, pointing to the need for T_4 in calculations.[55,56] Infinite order methods are particularly important today as investigators are pushing CC methods even to metals where no band-gap exists, while perturbative ones can only be applied carefully and with caveats.

F. Role of connected T_4 excitations.

The characteristic differences between odd-ordered connected clusters like T_3 and even-ordered ones like T_4 lead to different types of approximations that can be made. Assuming T_5 and higher are set to zero, the best that one can do at the level of T_4 is CCSDTQ.[52] The quasi-linearized form of higher-order CC equations can be conveniently written down and numerically evaluated by using $\overline{H}$ intermediates as shown elsewhere,[57] and in detail.[11] But for our purposes here, the lead terms are the ones that matter, analogous to the T_3 discussion. Focusing on them,

$$\begin{aligned} Q_4D_4T_4|0\rangle = Q_4\overline{H}|0\rangle =& Q_4(W_0T_2^2/2+W_{+1}T_3+W_{-2}T_2^3/3! \\ &+W_0T_4+W_{-1}T_3T_2+W_0T_3T_1+\ldots)|0\rangle_C \end{aligned}$$

the first two terms are third-order while the next four are fourth-order. In particular, the fourth term that represents T_4 into T_4, will lead to an $\sim$m^{10} computation. Except for CCSDTQ itself, we will initially exclude it and the other fourth-order terms. Thus, we obtain the third–order $T_4^{[3]}$ contribution,

$$Q_4D_4T_4^{[3]}|0\rangle = Q_4(W_0\frac{T_2^2}{2}+W_{+1}T_3)|0\rangle_C \tag{84}$$

composed of two parts, due to T_2 and T_3.

Thus, this $T_4^{[3]}$ connected quadruple quantity can directly contribute to $T_2^{[4]}$ after operation by W_{-2} and division by the D_2 denominator associated with the $T_2^{[4]}$,

$$Q_2T_2^{[4]}|0\rangle = Q_2\frac{W_{-2}}{D_2}\frac{Q_4}{D_4}T_4^{[3]}|0\rangle \tag{85}$$

Hence, the fifth-order energy arising from $T_4^{[3]}$ becomes,

$$E_Q^{[5]} = \langle 0|\frac{W'_{-2}}{D'_2}T_2^{[4]})|0\rangle_C = \langle 0|\frac{W'_{-2}}{D'_2}Q_2\frac{W_{-2}}{D_2}Q_4\frac{T_4^{[3]}}{D_4})|0\rangle_C \tag{86}$$

after applying the $\frac{W'_{-2}}{D'_2}$ term to $T_2^{[4]}$.

This is a place where a diagrammatic understanding of this expression is extremely valuable. Since $\frac{W_2}{D_2}$ and $\frac{W'_2}{D'_2}$ are equivalent second-quantized operations, they can be applied in either order in the above algebra. That means the diagram equivalent of Eqn. 86 can be drawn in two equivalent ways depending on the sequence (i.e., 'time-order') of the last two interactions. In one, $D_2 = (f_{ii}+f_{jj}-f_{aa}-f_{bb})$. In the other, it is replaced by $D'_2 = (f_{kk}+f_{ll}-f_{cc}-f_{dd})$. Since, $D_4 = f_{ii}+f_{jj}+f_{kk}+f_{ll}-f_{aa}-f_{bb}-f_{cc}-f_{dd}$,by writing these two equivalent algebraic terms preceded by $\frac{1}{2}$, one can invoke the factorization theorem of MBPT[11] and put all over a common denominator,

$$\frac{1}{2}[(\frac{W_2}{D_2}\frac{W_2'}{D_2'}\frac{T_4^{[3]}}{D_4})+(\frac{W_2'W_2}{D_2'D_2}\frac{T_4^{[3]}}{D_4})]_C = \frac{1}{2}\frac{[W_2W_2'T_4^{[3]}(D_2+D_2')]}{D_2D_2'D_4} \quad (87)$$

$$E_Q^{[5]}(T_2+T_3) = \frac{1}{2}[\frac{W_2W_2'(T_4^{[3]})}{D_2D_2'}] \quad (88)$$

and magically, the D_4 denominator disappears! The critical quantity in CC computations is the denominator, D_4, as its eight terms necessitate an $\sim$m^9 computational procedure unless it can be rigorously removed as done here. In this way, the $E_Q^{[5]}(T_2+T_3)$ quantity that is the full fifth-order contribution due to connected T_4 can now be evaluated with only a non-iterative $\sim$m^7 computation. That is the same level as (T) or the iterative CCSDT-3. The evidence that this is a very good approximation for T_4 on top of CCSDT and CCSDT-3 compared to FCI is shown elsewhere.[58] The combined CCSD(TQ) $\sim$m^7 approximation where this approximation for fifth-order $E_Q^{[5]}(T_2+T_3)$ is added to the prior fourth-order (T) approximation in CCSD(T) is less accurate, likely because of mixing different orders.

Once one has $T_4^{[3]}$,one can follow its indirect contribution to T_3,that arises from $T_2^{[5]}$,

$$Q_3D_3T_3^{[4]}|0\rangle = Q_3(W_{-1}T_4^{[3]}+f_{-1}T_4^{[3]})|0\rangle_C \quad (89)$$

$$Q_2D_2T_2^{[5]}|0\rangle = Q_2(W_{-1}T_3^{[4]}+f_{-1}T_3^{[4]})_C \quad (90)$$

$$Q_1D_1T_1^{[5]}|0\rangle = Q_1(W_{-2}T_3^{[4]})_C \quad (91)$$

It will contribute to sixth- and higher-order energies.

The above development but limited to just the T_2 part of $T_4^{[3]}$ is the cornerstone for what we call the 'ultimate T_2 model'. The origin of electron correlation arises from double excitations, making such an ultimate T_2 method a reference that deserves attention.

This fact is also pertinent to the recent interest in pCCD,[59–65] which is a limitation of CCD to just its spin-paired diagonal terms like $t_{I,\bar{I}}^{A\bar{A}}$ for closed shells, where the orbitals I and A are meant to be variationally optimum. Such an approximation is not orbitally invariant, nor 'insensitive' as in CCSD and this freedom is exploited to improve the approximation. The original derivation of Cullen[59] used CCD theory to derive GVB wavefunctions by restricting the T2 amplitudes to just the pair form and follow with an orbital optimization. As is well-known, such 'geminal' wavefunctions can describe some types of bond breaking that is more difficult in RHF CC calculations, though UHF CC does much better. That such a method can introduce geminal character into CC theory offers an alternative route toward describing certain non-dynamic correlation features that only scale as $\sim$m^4 like HF. See[66] for a recent critical study for excited states where the alternative tailored single-reference pCCD+TCCSD, is used, that is meant to exploit the pCCD kernel augmented by the rest of the CCSD terms. This has the advantage that it is solely a single-reference approach for bond-breaking problems where most would think some kind of MR-CC should be used. But, via pCCD, some non-dynamic correlation effects can be introduced and there is no need to introduce an active orbital MR space.

A different take on our ultimate T_2 follows from the expectation value, XCCD expression,[67]

$$E_{XCCD} = \langle 0|(\exp(T_2^\dagger)H\exp(T_2))|0\rangle_C \quad (92)$$

whose variational optmization would be VCCD. Now, $\exp(T_2^\dagger)$ introduces different terms than just those in CCD, like T_4.

$$E_{XCC}^{[5]}(T_2) = \frac{1}{4}\langle 0|(T_2^{\dagger^{[1]}})^2W_0(T_2^2)^2|0\rangle_C \quad (93)$$

where the $T_2^{[1]}$ terms are generalized first order. But for the T_2 part, this is equivalent to the $E_Q^{[5]}(T_2)$ expression we just derived although there is no D_4 denominator to remove. In fact, this expression was the origin of the simplified T_4 expression above, and attests to XCCD introducing new terms that do not occur in CCD.

If we want to incorporate either expression into an infinite-order CCD-like method, we define a 'factorized' version, Q_f,

$$Q_2Q_f = Q_2(T_2^\dagger)W_0(T_2)^2/2|0\rangle_C$$

$$Q_2D_2T_2|0\rangle = Q_2(W+W_0T_2+W_{-2}T_2^2/2+(T_2^\dagger)W_0(T_2)^2/2|0\rangle_C \quad (94)$$

and add it to the rest of the CCD equations to provide an infinite-order solution that is correct through fifth-order in doubles and quaduples. This expression is now applicable to any order T_2 amplitude instead of the first-order $T_2^{[1]\dagger}$ version above that is specific to fifth-order.

Going to the next term in an ultimate T_2 method, consider the sixth-order term that arises from just T_2 in the T_4 equations, namely

$$Q_4D_4T_4^{[4]}|0\rangle = Q_4W_{-2}T_2^3/3!|0\rangle \quad (95)$$

that is similarly processed into the sixth-order energy,

$$E_Q^{[6]}(T_2) = \langle 0|\frac{W_{-2}'}{D_2'}Q_2\frac{W_{-2}}{D_2}\frac{Q_4}{D_4}T_4^{[4]}|0\rangle \quad (96)$$

$$= \frac{1}{2}(\frac{W_{-2}'}{D_2'}+\frac{W_{-2}}{D_2})(\frac{Q_4}{D_4}T_4^{[4]}|0\rangle \quad (97)$$

$$= \frac{1}{2}(\frac{W_{-2}W_{-2}'}{D_2D_2'}Q_4T_4^{[4]}) \quad (98)$$

where the D_4 denominator is again eliminated by the factorization theorem. Note, this too, is equal to

$$E_{XCC}^{[6]}(T_2) = \frac{1}{12}\langle 0|(T_2^{[1]\dagger})^2W_{-2}T_2^3|0\rangle \quad (99)$$

Higher-even orders from hextuples like $E_H^{[8]}$ can be similarly added.

For hextuples, the lead fifth-order terms come from

$$Q_6D_6T_6^{[5]}|0\rangle = Q_6(W_0T_4T_2+W_{-2}T_2^4/4!+W_0T_3^2/2)|0\rangle \quad (100)$$

where the T_3 is not relevant to an ultimate T_2 method. T_4 is, in the sense it comes from Q_f, evaluated solely from T_2.The same will apply to combinations of $T_2,T_4,T_6,$and higher even orders.

A detailed study of the ultimate T_2 method is presented elsewhere.[68]

Note the XCCD expression offers an upperbound to the exact energy for any choice of T2, if there is no truncation. To describe 'strong correlation' one would hope to be able to evaluate such variational, untruncated exponential expressions (VCCD) in closed form.

The next potential step in an ultimate T_2 model is the transition to its unitary form,[69]

$$\tau = T_2 - T_2^\dagger \quad (101)$$

$$UCC = \exp(\tau)|0\rangle \quad (102)$$

$$\langle 0|\exp(-\tau)\exp(\tau)|0\rangle = 1. \quad (103)$$

$$E_{UCC} = \langle 0|\exp(-\tau)H\exp(\tau)|0\rangle \quad (104)$$

$$= \langle 0|\exp(\tau)^\dagger H\exp(\tau)|0\rangle \quad (105)$$

Now, expectation values are simply

$$\langle 0|O|0\rangle = \langle 0|\exp(-\tau)O\exp(\tau)|0\rangle \quad (106)$$

with no denominator. In both XCC and UCC, the expectation value form does not terminate, requiring some kind of truncation to provide useful approximations like UCC(4).[70] .Unlike normal CC/MBPT, UCC satisfies the Hellman-Feynmam condition above for properties, making the determination of analytical gradients much easier than in standard CC, a strong recommendation for their further development, along with their ready application on quantum computers. Note, $[T_2^\dagger, T_2] \neq 0$, complicating UCC compared to XCC, since both terms occur on the same side of the UCC expressions.

Without dwelling on too many numerical results, most of the above results with triples and quadruple terms compare on average with the known, small molecule FCI results as shown in Fig. 5. The valence only BH only has four electrons so CISDTQ is exact. Larger molecules would tend to show pretty well converged results at the CCSDTQ level, but not at the CISDTQ level because of the latter's unlinked diagrams and upper bound property. The improvement between finite-order MBPT and infinite-order CC is as expected. The poorness of CISDT is notable, as the largest error in CI after CISD arises from $C_4 \sim \frac{1}{2}T_2^2$.

G. Equation of Motion Coupled-cluster Theory:

So far, everything discussed has pertained to describing electron correlation in a single state, usually the ground state, but can be any state of the lowest symmetry, perhaps a broken symmetry one, or even an excited state of the same symmetry as the ground state if the starting single determinant reference is good enough.[71] But such a method is severely limited if one's objective is a spectrum of electronic states. The solution to this problem is the EOM-CC method.[72–74]

The concept is very simple. One simply considers two solutions of the time-independent Schrödinger equation, one for the ground state, Ψ_G, and for a second excited state, Ψ_X.

$$(H - E_g)\Psi_G = 0 \quad (107)$$

$$(H - E_X)\Psi_X = 0 \quad (108)$$

$$|\Psi_G\rangle = \exp(T)|0\rangle \quad (109)$$

The next step is to exploit the fact that the excited state, $\Psi_X = \Omega_X\Psi_G$, can be created with an excitation operator,

$$\Omega_X = r_X^0 + (r_{X1}\Omega_1 + r_{X2}\Omega_2 + ...) \quad (110)$$

$$r_{X1}\Omega_1 = \sum r_i^a\{a^\dagger i\} \quad (111)$$

$$r_{X2}\Omega_2 = \sum r_{ij}^{ab}\{a^\dagger i b^\dagger j\} \quad (112)$$

$$.. \quad (113)$$

operating onto the ground CC state. Of course, there is no restriction as the ultimate excited state would be the FCI for the target state. Then a little algebra shows that

$$[\overline{H},\Omega]|0\rangle = (\overline{H}\Omega)_C|0\rangle = \omega_X\Omega|0\rangle \quad (114)$$

$$\omega_X = E_X - E_G \quad (115)$$

where $[T, \Omega] = 0$, allows moving exp($\pm$T) inside of Ω, leaving us with the EOM CI-like eigenvalue equation for the X state. The ground state correlation is used to build $\overline{H} = \exp(-T)H\exp(T)$, and then the target state is obtained by appropriate projection to define the individual excitation operators. For the example shown, the excitation operators (1h,1p), (2h,2p), (3h,3p),... provide excited states of the same particle number as the ground state and are not limited to states of different symmetry than the ground states, as r_X^0 formally allows for the same symmetry. More completely, this model is called EE-EOM-CC for 'excitation energy' EOM-CC.

If we want a spectrum of principal ionized states, the operators of interest would be (1h,0p), (2h,1p), (3h,2p), etc. And the reverse for electron attached states. For double ionizations, (2h,0), (3h,1p), (4h,2p), ... Hence, to obtain the target state requires projection onto the same (nh, mp) determinants, and the latter defines the rank of the EOM matrix and its computational scaling. All calculations directly provide the energy difference instead of having to subtract between two large numbers as some approaches would require. They are termed IP-EOM-CC, EA-EOM-CC, DIP-EOM-CC and DEA-EOM-CC, e.g.

VII. Evolution toward simplicity requires direct calculations of energy differences.

For properties the model for EOM-CC is the same as the single state CC calculation as both are built upon an $\overline{H}$ that is non-Hermitian. Such operators have both left- and right-hand eigenvectors that are bi-orthogonal to exhaust their Hilbert space,

$$(\overline{H}R_X)_C = \omega_X R_X \quad (116)$$

$$L_X\overline{H} = L_X\omega_X \quad (117)$$

though the eigenvalues are the same. Thus, to evaluate the dipole strength, O=$\overrightarrow{\varepsilon} \cdot \overrightarrow{r}$,

$$\langle O \rangle = |\langle 0|L_X \overline{O} R_X|0\rangle| \tag{118}$$

Note this is directly analogous to the CC ground state solution where Λ has the role of L and R becomes unity. A slightly more general expression for the transition moment can be derived from the dynamic polarizability[75]. It adds to the above a quadratic term that arises from the CC non-linear equations. The numerical effect is small for any single molecule, but the latter approximation will scale correctly to all repeated units.

Excited states can be roughly characterized as in Fig. 7. From a closed shell ground state, most allowed excitations are to open-shell singlets, with the coordinate Ms=0 triplet states symmetry forbidden. In addition, there are excited states that are dominantly composed of double excitations sometimes called 'dark' states since they have little or no oscillator strength since doubly excited states cannot mix with a closed shell reference over a one-particle transition operator regardless of spectroscopic symmetry considerations.

In terms of excitation energies, the performance of EE-EOM-CCSD is shown in Fig. 8 compared to the iterative, EE-EOM-CCSDT-3 values, where the CCSDT-3 ground state is augmented by its excited state counterpart. These results are for the Mülheim data set.[77] These excited states are mostly allowed, singlet excited states, and provide a mean absolute error of 0.15 eV, all above the reference result. Close inspection of the plot shows that there are a few outliers that one would assume are from excited states dominated by doubly excitations. It is known that such states are less accurately treated at the EOM-CCSD level than the usual allowed excited states. requiring at least triple excitations, given by

$$Q_3 D_3 R_3^{[2]}|0\rangle = Q_3(\overline{HR}_2|0\rangle + \overline{HR}_1)_C|0\rangle \tag{119}$$

since the right-hand side has to be connected. But whereas the $\overline{R}_2$ term starts with (W$\overline{R}_2$)$_C$ and (f$\overline{R}_2$) in second-order, the only connected contribution from the presumably more important R_1 term arises from the three-body part of $\overline{H}$ that makes the term an order higher. Hence, the fourth-order correction to EOM-CCSD is

$$E_T^{[4]} = \langle 0|L_2 W R_3^{[2]}|0\rangle + \langle 0|L_1 W R_3^{[2]}|0\rangle + \langle 0|L_2 f R_3^{[2]}|0\rangle \tag{120}$$

Adding this term provides the result in Fig. 9 where the mean absolute error is reduced to 0.06 eV, and there are no obvious outliers.

Note the three fourth-order terms that constitute this EOM $E_T^{[4]}$ in 10 are the same terms that occur in $\Lambda CCSD(T)$ except T_3 replaces R_3, and $\Lambda_1$and Λ_2 replace L_1 and L_2. For CCSD(T), Λ_1 and Λ_2 are further approximated by $T_1^\dagger$ and $T_2^\dagger$. A proposed improvement to EOM-CCSDT-3 has been presented by Matthews and Stanton[78] emphasizing the shape of excited state PES, along with excitation energies.

The issue of dark states warrants some discussion, as this has been a well-known failing of EOM-CCSD's spectrum. One would need to identify such doubly excited states and assign them larger error bars compared to the normal allowed states. Once triples are added at the level EOM-CCSDT, the errors are significantly reduced, but CCSDT/EOM-CCSDT is an ~m^8 computation compared to CCSD's ~m^6. Simpler triples models like EOM-CCSD(T) and EOM-CCSDT-3 are non-iterative and iterative, ~m^7 and are often sufficient. Arguments can be made for EOM-CCSDTQ as the best viable 'predictive' level, though at an ~m^{10} scaling.

Whereas the role of R_2 in EOM-CCSD is to relax the dominantly R_1 amplitudes in describing allowed singlet states–a necessity for accurate results—for doubly excited states R_3 plays the same role for states dominated by R_2. To illustrate, Loos, et al[79] have identified several molecules that have such doubly dominated, dark states and reported EOM-CCSDT and some EOM-CCSDTQ results.

For this collection of states, the % R_2 at the EOM-CCSD level is shown in Fig. 11, emphasizing the dominant role of R_2.The results from several levels of EOM are shown in Fig. 12, demonstrating errors of EOM-CCSD for such states to vary from ~2-6 eV, but once triples are added, even at the ~m^7 level the results are much improved.

The new method also shown is termed the intermediate state (IS) approach that provides dark state spectral energies limited to IS-EOM-CCSD at its ~m^6 cost. The procedure is illustrated in Fig. 13 where an open-shell reference determinant is used subject to symmetry tailoring to ensure that the two determinants involved have the same ± amplitudes depending upon whether the IS is an Ms=0 triplet or an open-shell singlet. Regardless, the dark state excitation energy is much improved, with or without tailoring, even compared to the ~m^7 triple excitation methods. This augmentation provides a EOM-CCSD level approach that is equally good for doubly excited states as it usually is for the allowed singlet excitations, but not in one calculation. Hence, it does not provide one method that is equally good for all states. That is more likely to be the ~m^7 EOM-CCSDT-3 or Matthews and Stanton, or CC3[80] for the time being.

H. Time dependent EOM-CCSD

The next notable development in EOM-CC over the last few years has been achieved by choosing to use time-propagation to obtain an (TD)-EOM-CC spectrum[81–83] as opposed to the standard matrix diagonalization approach. The numerical results are the same to within their different computational errors, but the two alternatives offer complementary ways to generate spectra. In the time-dependent approach one propagates the dipole moment operator in the Heisenberg form,

$$\Theta(t)|0\rangle = [\exp(H^{(0)})\Theta\exp(-H^{(0)}t)] \tag{121}$$

to act on the ground state CC wavefunction,

$$\Theta(t)\exp(T)|0\rangle = [\exp(H^{(0)})\Theta\exp(-H^{(0)}t)]\exp(T)|0\rangle \tag{122}$$

Left multiplication by exp(-T) provides $\overline{\Theta} = \exp(-T)\Theta(t)\exp(T)$,whose time-derivative is

$$i\frac{d\overline{\Theta}(t)}{dt}\exp(T)|0\rangle = -[H^{(0)}, \overline{\Theta}(t)|0\rangle \tag{123}$$

to give the right-hand propagation. The corresponding left-hand

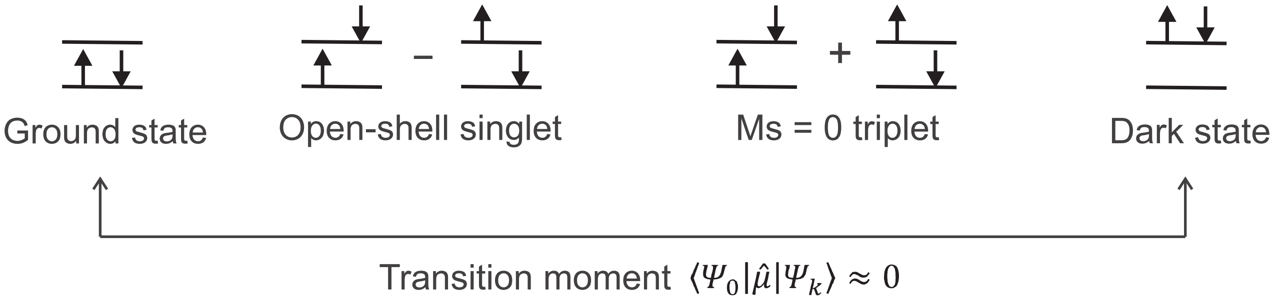


Fig. 7 Depiction of zeroth-order excited states.

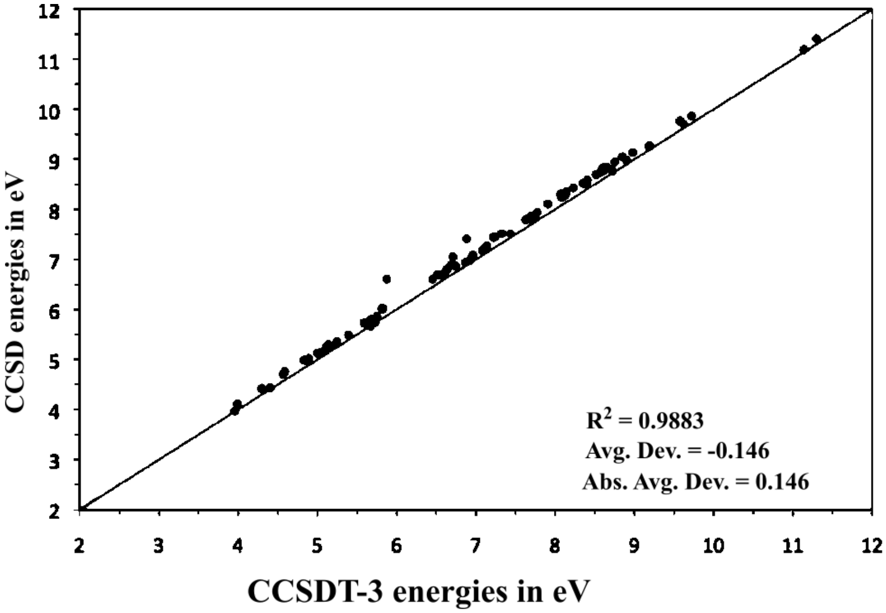


Fig. 8 Error comparison between EOM-CCSD and EOM-CCSDT-3[76]

propagation is

$$i\langle 0|(1+\Lambda)\frac{d\overline{\Theta}(t)}{dt} = -\langle 0|(1+\Lambda)[H^{(0)},\overline{\Theta}(t)] \quad (124)$$

Integrating either provides $\overline{\Theta}(t)$ at any time interval (usually chosen to be 0.01) relative to the initial value at t=0. The two overlaps,

$$\langle 0|(1+\Lambda)\overline{\Theta}(0)|\overline{\Theta}(t)|0\rangle \quad (125)$$

$$\langle 0|\Lambda\overline{\Theta}(t)|\Theta(0)|0\rangle \quad (126)$$

are the auto-correlation functions.

To illustrate its application, consider the full spectrum of the water molecule and its cation in TD-EOM-CCSD from the core excitations on the extreme right to the valence excitations on the left of the Fig.14 By construction, only dipole allowed states are obtained.

Of course, the same procedure can be used with other transition operators to provide other parts of a spectra. This is illustrated by a study of quadrupole transitions.[84] Another useful generalization of TD-EOM-CC is to select a 'tailored' probe of a particular frequency and observe a molecule's behavior over time. This ties closely with the pump-probe experiments being conducted in atto-second spectroscopy.[85]

I. One electron spectrum from IP and EA-EOM-CCSD

If we simply replace the R_1,R_2 and L_1,L_2 operators in the EE-EOM-CC equations by operators that remove an electron, like 1h0p, 2h1p, 3h2p..., meaning $R_K^{IP} = R_{iK}\{i^\dagger\} + R^a_{ijK}\{i^\dagger j^\dagger a\} + R^{ab}_{ijkK}\{i^\dagger j^\dagger k^\dagger ab\} + ...$and sum over repeated indices we obtain the IP-EOM-CC equations. Doing the same for 0h1p, 1h2p, 2h3p,...we obtain the EA-EOM-CC equations. Diagonalization of $\overline{H}$ then gives the $\{\omega_K\}$ for each state, and to the degree the state is dominated by an orbital index, $\{i^\dagger\}$,or$\{a\}$, an easy orbital interpretation. This is the basis for what we call correlated orbital theory (COT),[86] as these orbitals reflect the electron correlation put into the IP/EA-EOM equations while providing bi-orthogonal sets of eigenvectors. Thus, in addition to HF and Kohn-Sham, another single determinant form is obtained from COT. Hybrids of COT with elements of KS-DFT lead to the QTP functionals[87] we have proposed that are meant to emulate the results of IP/EA-EOM-CC in inexpensive calculations.

There is a seamless connection between the electronic excited states from EE-EOM-CC and those where one electron has been excited to give the IP-EOM-CC values or added to obtain the EA-

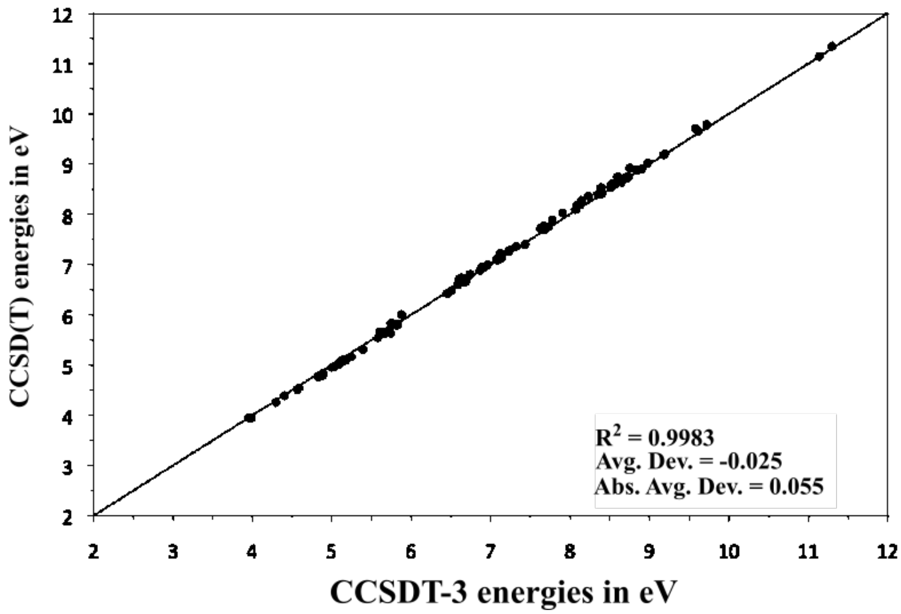


Fig. 9 Error comparison between EOM-CCSD(T) and EOM-CCSDT-3

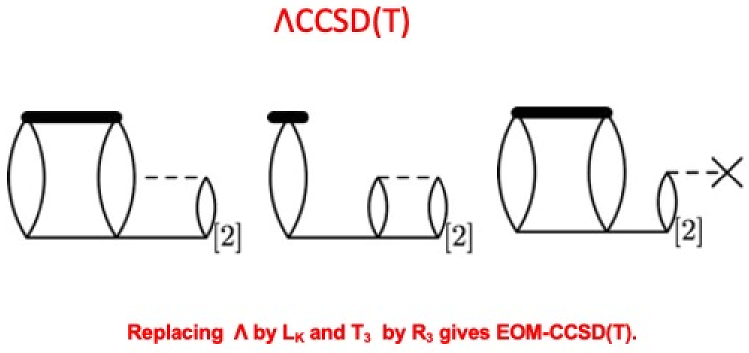


Fig. 10 Three Terms that Define CCSD(T), ΛCCSD(T), EOM-CCSD(T)

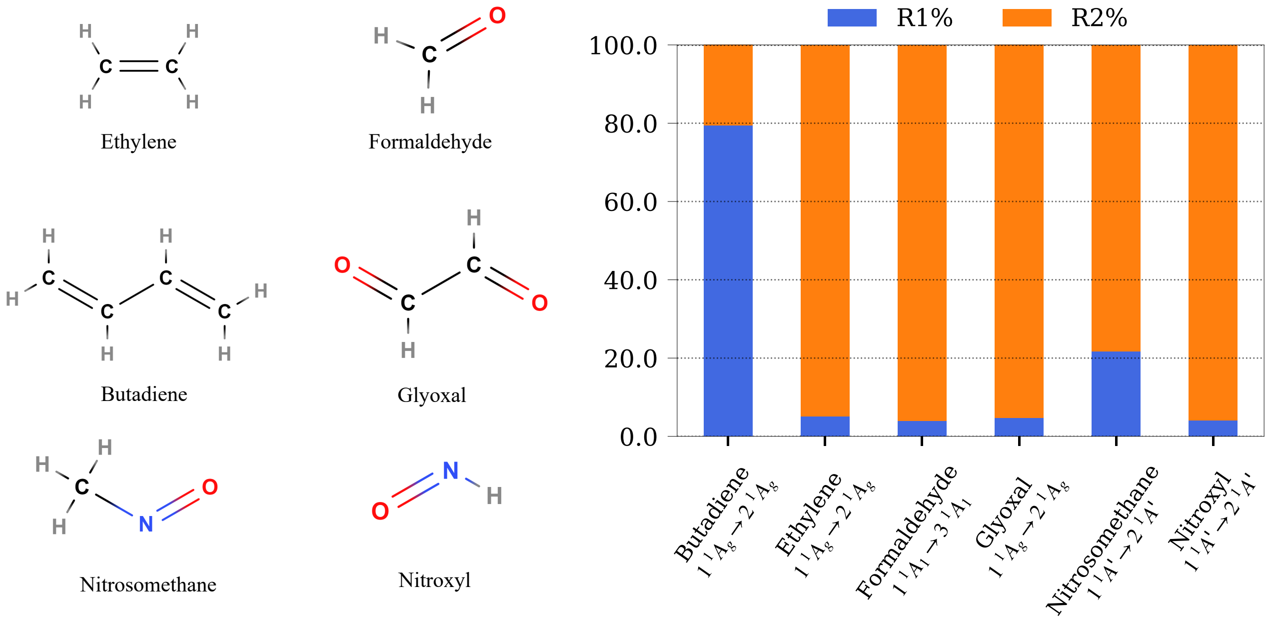


Fig. 11 Example of molecules with varying extents of population in the R_2 vector.

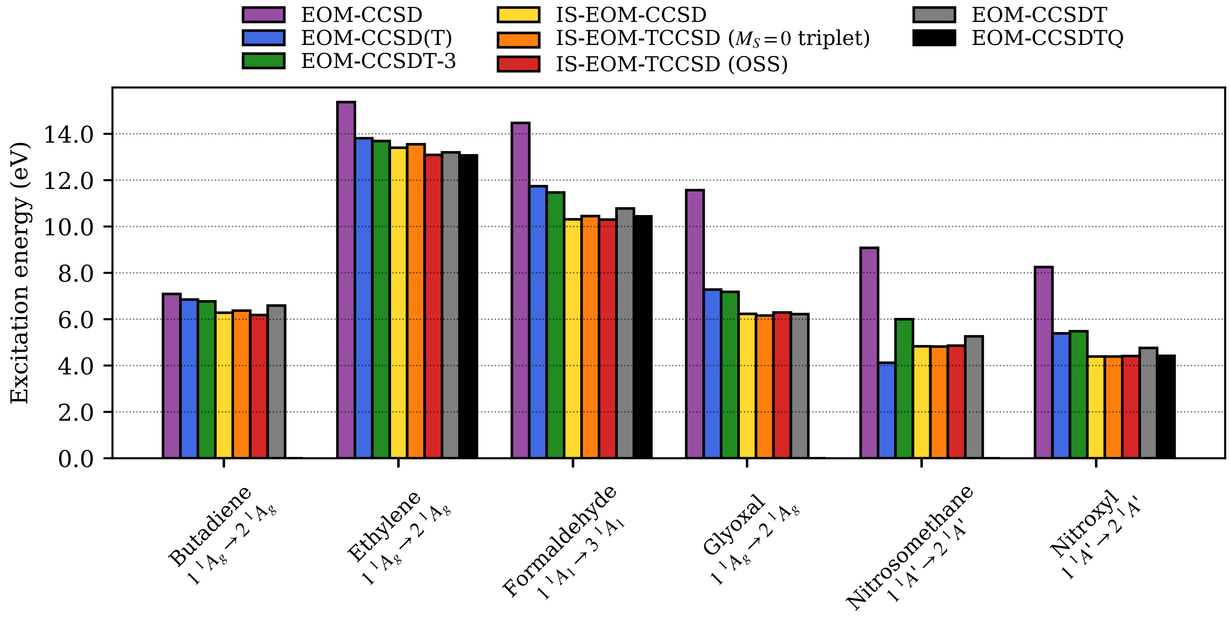
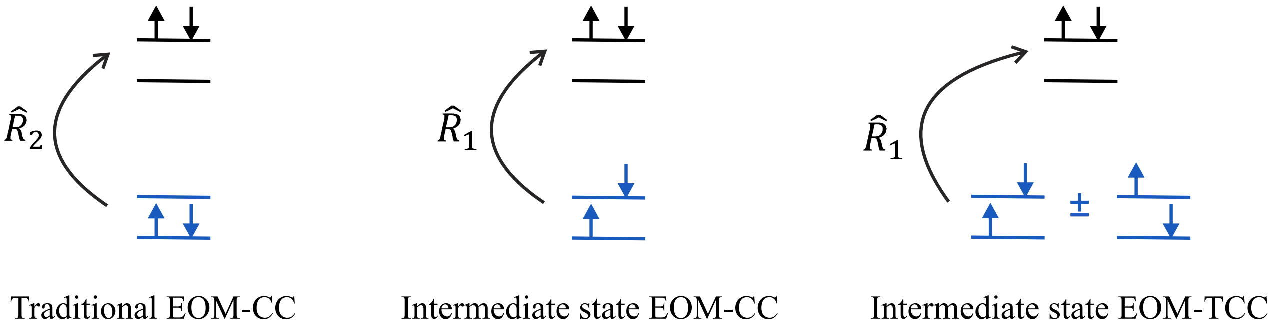


Fig. 12 Error comparison of various methods targeting the dark states.



Traditional EOM-CC Intermediate state EOM-CC Intermediate state EOM-TCC

Fig. 13 Intermediate state EOM-CC scheme.

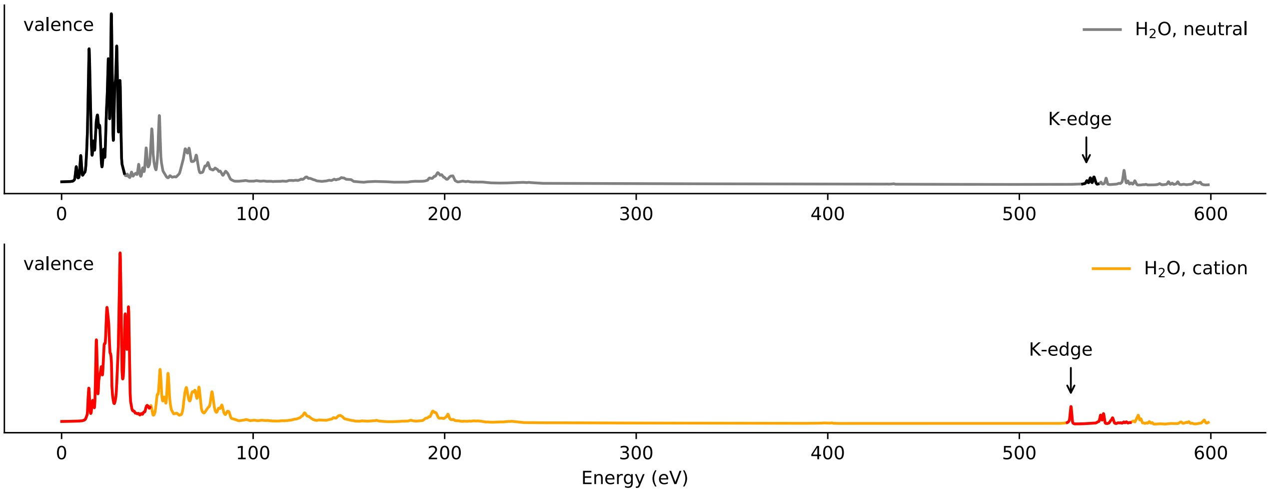


Fig. 14 Depiction of water molecule spectra.

EOM-CC values. One can observe this fact from simply adding a zero gaussian function into the basis set in an EE calculation[88,89] as an approximation to a continuum function that will accommodate the extra electron leaving the IP's for the N-electron problem as the new eigenvalues to the EE-EOM-CC problem for N-1 electrons. The reverse will provide the EA's. This rigorous, seamless connection between ionized and excited electronic states is not satisfied by most quantum chemical calculations, but must be in EOM-CC.

Generalization to double ionizations and double electron attachment processes follow in the same way by considering 2h0p, 3h1p,4h2p,,,terms in R^{DIP} and L^{DIP} and the opposite 0h2p 1h3p, etc. for DEA. These DIP/DEA-EOM methods also have an important role in rigorously describing multi-reference problems subject to a complete active space of two electrons in two orbitals[90] within a standard single reference CC/EOM computational framework. Formally, TIP and TEA would do the same for a space of three electrons in three orbitals.[91]

VIII. A Seamless connection between excited states and ionized, doubly ionized (DIP), and electron attached, and doubly attached (DEA) states is another requirement of the evolution toward simplicity.

As discussed with reference to the energy of an infinite system like a polymer having to be extensive (scale with N) to be meaningful, the energy difference (excitation energy) between two such states that scale with N, has to be N independent, i.e., *size-intensive*. This important property is ensured by EOM-CC. A further consequence is that EE-EOM-CC excited states for a molecule like, AB*, separating into fragments, have the size-intensive property, AB* $\mapsto A^* + B, A + B^*$[92] Just as extensivity is critical to quantum chemical calculations, the corresponding 'intensive' property is, too, where the excitation energy difference is localized somewhere in the molecule. This property ensures accurate relative energy differences that reflect the local excitation in a large complicated molecule. Ideally, the intensive value would correspond to the difference between two properly extensive results as assumed above, but that is not always necessary, as a non-extensive CIS result still provides intensive excitation energies. For very large polymeric systems where there is a charge-transfer excitation between the two ends of the chain, one would want an extensive method to account correctly for size and an intensive method to account for the localized energy difference consisting of an IP at one end and an EA at the other.

IX. The evolution toward simplicity requires that quantum chemical methods provide properly size-intensive numerical results for local excitations, as does EOM-CC.

To take this example all the way, it would be nice if AB$\hookrightarrow A^+ + B^-$ as well as the size-intensive property above. But as mentioned earlier, charge transfer separability (CTS) is not assured by EE-EOM-CC for charge-transfer. The origin of this formal discrepancy in that the EE-EOM-CC equations are CI-like, instead of depending upon an exponential ansatz for the target wavefunction. Though all expressions are connected, this failure shows up in the eigenvalues.[93] The effect is numerically small even at the EOM-CCSD level, and much smaller once triples are included, but is not 0. Methods like Fock space (FS-MRCC)[94,95] and STEOM-CC,[96] fix this problem being both extensive, intensive, and charge-transfer separable, as their exponential ansatze pertains to both the ground and excited states. But neither are exact for two electrons, unlike CC/EOM. Note the fact that IP/EA-EOM-CC is seamless with EE-EOM-CC for excited states does not ensure CTS for a given charge-transfer excited state can be decomposed into those two terms, except at complete separation where the residual coupling terms that give rise to this CTS issue have to vanish.

X. A further desirable property would be a seamless transition to AB$\hookrightarrow A^+ + B^-$, but CC/EOM-CC without modification does not have this property. EOM-CC$_X$[93] restores it as does STEOM-CC and FS-MRCC.

J. Electron Propagator

The electron propagator (Greens' function)[97,98] offers a seemingly different approach to the direct determination of energy differences. It is defined as

$$\begin{aligned}G_{pq}(\omega) =&\langle\Psi_0|p^\dagger(\omega-E_0+H)^{-1}q|\Psi_0\rangle\\&+\langle\Psi_0|q(\omega-H+E_0)^{-1}p^\dagger|\Psi_0\rangle\\=&\sum_\mu\Bigg(\frac{\langle\Psi_0|p^\dagger|\Psi_\mu^{N-1}\rangle\langle\Psi_\mu^{N-1}|q|\Psi_0\rangle}{\omega-(E_0+E_\mu^{N-1})}\\&+\frac{\langle\Psi_0|q|\Psi_\mu^{N+1}\rangle\langle\Psi_\mu^{N+1}|p^\dagger|\Psi_0\rangle}{\omega-(E_\mu^{N+1}+E_0)}\Bigg)\end{aligned}\tag{127}$$

Its poles define ionization potentials when $\omega=(E_0+E_\mu^{N-1})$ and electron attachment when $\omega=(E_\mu^{N+1}+E_0)$. The residue at the poles defines the transition moments. Note the two parts of the propagator, the IP part and the EA part, are coupled with both being required to obtain any solution of $\mathrm{G}(\omega)=\omega$. The latter becomes the Dyson equation when reduced to a one-particle form with the addition of the self-energy, $\Sigma(\omega)$, to describe electron correlation, $\mathrm{h}_D(\omega)=f+\Sigma(\omega)$. Its eigenvectors are Dyson amplitudes (not orbitals). The philosophy of Greens' functions is to de-emphasize the importance of the complicated ground state solution given by Ψ_0, in favor of the actual energy differences seen in experiments. This has often led to using an SCF function as an approximation to Ψ_0 for computational simplicity. But quite generally, amazing things happen once one formally inserts a CC wavefunction represented in Hilbert space into the electron propagator.[99,100] First, the frequency dependence of the operators disappears. This eliminates the coupling between the IP and EA parts of the propagator. Instead, one gets an exact decomposition of the propagator into the IP-EOM-CC and EA-EOM-CC problems with the frequency dependence showing up only as the eigenvalues, ω_K, for the particular Kth states,

$$(\overline{H}R_K^{IP})_C = \omega_K R_K^{IP} \tag{128}$$

$$(\overline{H}R_K^{EA})_C = \omega_K R_K^{EA} \tag{129}$$

Hence, in our evolution toward simplicity, all electron propagator methods could be viewed as approximations to the above simpler EOM-CC formulae that eliminates having to solve a $\mathrm{G}(\omega)=\omega$, problem in favor of the above eigenvalue solutions. As all CC and EOM-CC solutions are represented in Hilbert space, not the one-particle space of the frequency dependent Dyson approach, this suits the linear algebra solutions of the equations better than a root search as occurs in the Dyson case. This also means that the 'principal' IPs, meaning the energy required to remove an electron from any orbital without further orbital rearrangements are obtained first, while the subsequent shake-up roots that mix excitation energies with IP's that are other poles of the usual Dyson equation can be obtained from additional eigenvalues of $\overline{H}$ with further effort. All the roots are there that would occur in the Dyson equation, but now come conveniently in different orders. This is a major advantage of the IP/EA-EOM-CC formulation as the Dyson equation indiscriminately provides all possible roots.

A word about the polarization propagator[101] might be pertinent. Its objective is the treatment of electronic excited states and their transitions. This propagator is simply the frequency dependent polarizability[75] whose poles are the excitation energies and whose residue at the poles defines the dipole transition strength. This provides the alternative transition expression to the EOM form in Eqn. () for the transition moments. A normal polarization propagator would include particle-hole intermediate states often used with a HF ground state approximation to derive the RPA equations.[102] But like the electron propagator, inserting the CC ground state into the frequency dependent polarizability provides EOM-CC for excitation energies and dipole strengths. See also[103] for a CC discussion of the polarization propagator.

K. Relativistic corrections for coupled-cluster calculations

Obviously, 'predictive' accuracy demands an account of relativistic corrections on top of even FCI results for the Schrödinger equation. These apply to heavy atoms and the molecules or solids built from them. But even for light atoms various effects can be essential at times like the scalar relativistic corrections for core ionization and excitation and the pervasive spin-orbit effects essential in spectroscopy. All can be added rigorously by solving the many-body Dirac equation with coupled-cluster theory. This leads to the four-component solution of the Dirac equation made possible today by the DIRAC program[104] that offers the relativistic equivalent to the non-relativistic CC solutions.

In between the full four component treatment and non-relativistic calculations lie various possible approximations ranging from relativistic psuedo-potentials, to the evaluation of DMV (Darwin and Mass Velocity) corrections, to Douglas-Kroll-Hess,[105] to an exact two-component theory.[106,107] ACES2 uses fifth-order Douglas-Kroll (DKH5). CFOUR includes the exact two-component correction. To do relativistic corrections justice would require a thorough review, see[108]. Some comparative numerical results are shown elsewhere.[109]

More pertinent to this perspective is new CC work for spin-orbit effects, as EOM-CC has been formulated to provide direct spin-orbit corrections by adding the latter as a perturbation on top of non-relativistic CC ground and EOM-CC states,[110] implemented in ACES 3. The problem is illustrated in Fig. 15 and some results for methyl iodide are shown in Fig. 16. In this work, the basis set problem is further mitigated by using F12 basis set methods in the CC/EOM-CC calculations, as shown in Table 1. Note, there is also a nice and automatic treatment of double group symmetry for the spin-orbit states that is part of this EOM spin-orbit package.

A particularly important aspect of the F12 methods that fits our 'evolution toward simplicity', is that the current incarnation of this method employs the 'SP ansatz' which means it incorporates the mathematically rigorous properties of the correlation cusp in its equations.[8,9] This rectifies the failure of a gaussian basis' description of the cusp, the origin of much of the correlated basis set error in quantum chemistry. Hence, building in the exact cusp behavior in CC is currently the best way to solve this problem. One should always use exact conditions in quantum chemistry when possible. Perhaps, a simpler route would allow correcting for the cusp error with an analytic form that could be built into the second-quantized Hamiltonian from the start for all applications, but so far, no such universal option is available.

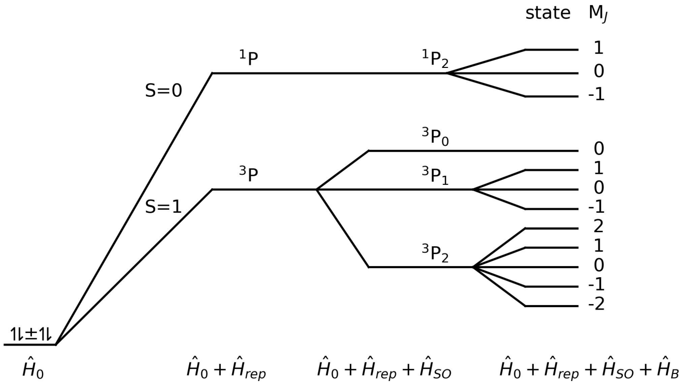


Fig. 15 Depiction of spin-orbit splittings

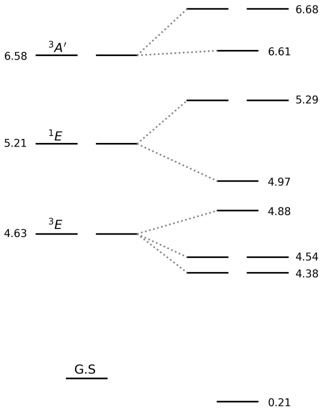


Fig. 16 Results for methyl iodide

Table 1 Electron affinities (in eV.) and corresponding splittings (Δ, in cm^{-1}) for different basis sets using regular (Reg.) and explicitly-correlated (F12) EA-EOM-CCSD

	AUG-CC-PCDZ		AUG-CC-PCTZ		AUG-CC-PCQZ		AUG-CC-PC5Z	CBS	Exp.[111]
	Reg.	F12	Reg.	F12	Reg.	F12			
Al^+		$\gamma = 3.1$		$\gamma = 3.8$		$\gamma = 4.3$			
$^2P_{1/2}$	5.8333	5.8565	5.9049	5.9140	5.9371	5.9420	5.9458	5.9549	5.986
$^2P_{3/2}$	5.8206	5.8435	5.8915	5.9004	5.9235	5.9283	5.9321	5.9411	
$\Delta_{3/2-1/2}$	102.42	104.84	108.07	108.89	109.68	110.49	110.50	111.30	112.10
NO^+									
$\Omega = 3/2$	9.3938	9.7377	9.6685	9.7911	9.7425	9.8000	9.7694	9.7976	9.262
$\Omega = 1/2$	9.3805	9.7241	9.6542	9.7767	9.7279	9.7853	9.7547	9.7828	
$\Delta_{3/2-1/2}$	107.43	109.80	115.24	115.97	117.67	117.93	118.64	119.60	123.1
$O_2{}^{2+}$									
$\Omega = 3/2$	23.9112	24.3839	24.2601	24.4222	24.3589	24.4342	24.3981	24.4393	24.14
$\Omega = 1/2$	23.8881	24.3606	24.2356	24.3276	24.3338	24.4092	24.3729	24.4139	
$\Delta_{3/2-1/2}$	186.02	188.69	198.78	198.94	202.02	202.25	203.56	205.17	200.3

L. Coupled-cluster theory for polymers and crystalline solids

The natural domain for applications of CC/EOM beyond molecules is to extended, indeed, infinite systems. This broad area defines the subject of solid-state or condensed matter physics, and only linked, size-extensive, many-body methods like CC, MBPT, or many-body Greens' functions or propagator methods are suited to describing electron correlation in infinite systems, as discussed earlier. The developments in solids are built upon translational symmetry and periodic boundary conditions, not the square-integral ones that pertain to finite atoms and molecules. This distinction might seem modest, but it had largely kept the two domains separate in terms of correlation until the late 90's, when at least MBPT2 correlation was added for 1D-polymers. Sun and I reported such results[112] in carefully converged calculations[113] that built upon three independent periodic HF programs that provided polymer SCF calculations as the reference for further electron correlation treatments.[114,115]

The other group from quantum chemistry to address the polymer problem was Hirata and Iwata,[116] whose initial emphasis was on analytical energy derivatives in polymers to optimize structures and to compute force constants, as one would do for molecules, but now at the MP2=(MBPT2) level. Hirata[117] generalized his and Sun's work to the treatment of electron correlation to include CCD and various approximations to it.

For extended systems, at this point, the framework was formally in place to treat 1D, 2D and 3D periodic systems subject to crystalline gaussian basis functions, but such calculations still required far more computational effort than molecules as one had to ensure convergence with the number of unit cells and the number of k-points in the first Brillouin zone. Also, one had to move to a complex orbital description that few quantum chemists had employed in their programs.

Other concerns pertained to the perceived linear dependence in the gaussian basis set that would have to occur for an infinite system. In fact, early practitioners,[118–120] felt that such CC calculations should use plane-wave basis sets that have the advantage that convergence with the number of plane waves can be controlled, but the disadvantage that they do not provide a good approximation for the mostly localized electrons in the component atoms where gaussians are far better. This typically forces plane wave calculations into using psuedo-potentials for the non-valence bands.

In the early years of the 21th century, serious CC/MBPT studies for infinite systems were beginning in earnest using crystalline Gaussian basis functions.[5,29] This development will continue to evolve until for the first time there will be a seamless connection between CC/MBPT calculations for molecules, for oligomers and increasingly larger clusters, and an ability to study convergence to the infinite limit using precisely the same tools. It should also be understood that contrary to conventional wisdom, even metals are accessible to CC/EOM as a band-gap is not a necessity to apply an infinite-order method. So most of the infinite-order approximations obtained from CC will be applicable. The likely exception will be a method like CCSD(T) where the triples part is treated perturbatively, as it implicitly expects a band gap in its applications, but switching to CCSDT-n that has the same physics and computational attractiveness as CCSD(T) but is infinite order should rectify the problem. As long as there is a band-gap CCSD(T) is imminently doable.

To see the current, impressive progress in CC/EOM-CC for infinite, periodic systems in 1D, 2D, and 3D,, see the work of Berkelbach,[121] Xiao Wang,[122] Xin Xing,[123] and others.[117] A typical calculation now will provide the band structure and the fundamental gap from IP/EA-EOM-CCSD, the optical and excitation spectra from EE-EOM-CCSD, and the detailed geometric structure of various phases from geometry optimization that might use the CC analytical derivative methods created for molecules, all discussed earlier in this perspective. Even modified Gaussian basis sets have been introduced for periodic systems[29] to help to moderate the basis set's linear dependency that once upon a time was thought to be a major problem for the use of finite basis sets like crystalline gaussians in infinite systems. It goes without saying that the eleventh component of the 'evolution towards simplicity' is

XI. A seamless connection between CC/EOM-CC for finite systems and the same for infinite ones. This is now a reality, and it portends many fundamental consequences for the field from the treatment of strong electron correlation, to phase transitions, to high-Tc superconductivity.

Conclusion

I hope this perspective has succeeded in documenting how CC/EOM theory, and its underlying 'many-body' framework, has enabled electronic structure theory to take a giant step forward. The eleven components identified as steps in the 'Evolution to Simplicity' are critical to the further advancement of quantum chemistry and they should serve as a template that should be assessed to identify worthy future developments. Combining these formally exact conditions with others that might be encountered, like the correlation cusp condition used in F12, guarantee genuine advances in the field.

To complete the circle, besides electronic structure, the CC method that was first conceived in nuclear physics by Coester and Kummel,[124] is now a prominent choice for application to nucleons using the tools and approximations first introduced in quantum chemistry,[125,126] that are discussed in this perspective.

In all its manifestations, coupled-cluster theory has dramatically changed the treatment of electron correlation, and its future contributions, on quantum computers and otherwise, will be remarkable!

Conflicts of interest

There are no conflicts of interest.

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Notes and references

1 R. J. Bartlett and M. Musiał, *Reviews of Modern Physics*, 2007, **79**, 291–352.
2 J. Paldus, *Theory and Applications of Computational Chemistry*, Elsevier, 2005, pp. 115–147.
3 R. J. Bartlett, *Theory and Applications of Computational Chemistry*, Elsevier, 2005, pp. 1191–1221.
4 R. J. Bartlett, Y. C. Park, N. P. Bauman, A. Melnichuk, D. Ranasinghe, M. Ravi and A. Perera, *The Journal of Chemical Physics*, 2020, **153**, 234103.
5 J. Yang, W. Hu, D. Usvyat, D. Matthews, M. Schütz and G. K.-L. Chan, *Science*, 2014, **345**, 640–643.
6 D. Claudino, *International Journal of Quantum Chemistry*, 2022, **122**, e26990.
7 J. K. Freericks, *Symmetry*, 2022, **14**, 494.
8 S. Ten-no, *The Journal of Chemical Physics*, 2004, **121**, 117–129.
9 D. Bokhan, S. Ten-no and J. Noga, *Physical Chemistry Chemical Physics*, 2008, **10**, 3320–3326.
10 R. J. Bartlett and G. D. Purvis, *International Journal of Quantum Chemistry*, 1978, **14**, 561–581.
11 I. Shavitt and R. J. Bartlett, *Many-body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory*, Cambridge university press, 2009.
12 P.-O. Löwdin, *International Journal of Quantum Chemistry*, 1968, **2**, 867–931.
13 J. D. Watts, J. Gauss and R. J. Bartlett, *The Journal of Chemical Physics*, 1993, **98**, 8718–8733.
14 R. J. Bartlett and M. Musiał, *The Journal of Chemical Physics*, 2006, **125**, 204105.
15 J. Paldus, J. Čížek and M. Takahashi, *Physical Review A*, 1984, **30**, 2193–2209.
16 K. Jankowski and J. Paldus, *International Journal of Quantum Chemistry*, 1980, **18**, 1243–1269.
17 R. A. Chiles and C. E. Dykstra, *The Journal of Chemical Physics*, 1981, **74**, 4544–4556.
18 W. Meyer, *International Journal of Quantum Chemistry*, 1971, **5**, 341–348.
19 A. C. Hurley, *Electron correlation in small molecules*, Academic Press, 1976.
20 V. Rishi and E. F. Valeev, *The Journal of Chemical Physics*, 2019, **151**, 064102.
21 M. Musiał and R. J. Bartlett, *The Journal of Chemical Physics*, 2007, **127**, 024106.
22 I. Purvis, George D. and R. J. Bartlett, *The Journal of Chemical Physics*, 1982, **76**, 1910–1918.
23 W. D. Laidig, G. D. Purvis and R. J. Bartlett, *International Journal of Quantum Chemistry*, 1982, **22**, 561–573.
24 S. Diner, J. Malrieu, P. Claverie and F. Jordan, *Chemical Physics Letters*, 1968, **2**, 319–323.
25 K. Ruedenberg, *The Journal of Chemical Physics*, 2022, **157**, 024111.
26 R. J. Bartlett, *Chemical Physics Letters*, 2009, **484**, 1–9.
27 J. A. Pople, M. Head-Gordon and K. Raghavachari, *The Journal of Chemical Physics*, 1987, **87**, 5968–5975.
28 J. D. Watts, M. Urban and R. J. Bartlett, *Theoretica Chimica Acta*, 1995, **90**, 341–355.
29 J. McClain, Q. Sun, G. K.-L. Chan and T. C. Berkelbach, *Journal of Chemical Theory and Computation*, 2017, **13**, 1209–1218.
30 J. J. Ladik, *Quantum Theory of Polymers as Solids*, Springer Science & Business Media, 2012.
31 M. Rittby and R. J. Bartlett, *The Journal of Physical Chemistry*, 1988, **92**, 3033–3036.

32 H. Sekino and R. J. Bartlett, *International Journal of Quantum Chemistry*, 1987, **32**, 487–493.

33 Z. W. Windom, A. Perera and R. J. Bartlett, *The Journal of Chemical Physics*, 2022, **156**, 204308.

34 J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865–3868.

35 V. Rishi, A. Perera and R. Bartlett, *Theoretical Chemistry Accounts*, 2014, **133**, 1515.

36 A. I. Krylov, C. D. Sherrill, E. F. C. Byrd and M. Head-Gordon, *The Journal of Chemical Physics*, 1998, **109**, 10669–10678.

37 A. G. Taube and R. J. Bartlett, *Collection of Czechoslovak Chemical Communications*, 2005, **70**, 837–850.

38 A. G. Taube and R. J. Bartlett, *The Journal of Chemical Physics*, 2008, **128**, 164101.

39 J. N. Byrd, V. F. Lotrich and R. J. Bartlett, *The Journal of Chemical Physics*, 2014, **140**, 234108.

40 M. Sparta and F. Neese, *Chemistry Society Reviews*, 2014, **43**, 5032–5041.

41 N. Flocke and R. J. Bartlett, *Chemical Physics Letters*, 2003, **367**, 80–89.

42 M. Schütz and H.-J. Werner, *The Journal of Chemical Physics*, 2001, **114**, 661–681.

43 J. Gauss, J. F. Stanton and R. J. Bartlett, *The Journal of Chemical Physics*, 1991, **95**, 2639–2645.

44 E. A. Salter, H. Sekino and R. J. Bartlett, *The Journal of Chemical Physics*, 1987, **87**, 502–509.

45 J. Noga and R. J. Bartlett, *The Journal of Chemical Physics*, 1987, **86**, 7041–7050.

46 J. Noga, R. J. Bartlett and M. Urban, *Chemical Physics Letters*, 1987, **134**, 126–132.

47 *A. C. Hurley in: Molecular Orbitals in Chemistry, Physics, and Biology: A Tribute to R. S. Mulliken*, ed. P.-O. Löwdin and B. Pullman, Academic Press, 1964, p. 578.

48 R. J. Bartlett, *Molecular Physics*, 2010, **108**, 2905–2920.

49 M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *The Journal of Chemical Physics*, 1985, **83**, 4041–4046.

50 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chemical Physics Letters*, 1989, **157**, 479–483.

51 J. D. Watts, J. Gauss and R. J. Bartlett, *The Journal of Chemical Physics*, 1993, **98**, 8718–8733.

52 S. A. Kucharski and R. J. Bartlett, *Journal of Chemical Physics*, 1998, **108**, 5243–5254.

53 A. G. Taube and R. J. Bartlett, *The Journal of Chemical Physics*, 2008, **128**, 044110.

54 Y. S. Lee, S. A. Kucharski and R. J. Bartlett, *The Journal of Chemical Physics*, 1984, **81**, 5906–5912.

55 S. A. Kucharski and R. J. Bartlett, *The Journal of Chemical Physics*, 1992, **97**, 4282–4288.

56 M. Musial and R. J. Bartlett, *The Journal of Chemical Physics*, 2010, **133**, 104102.

57 S. A. Kucharski and R. J. Bartlett, *Theoretica Chimica Acta*, 1991, **80**, 387–405.

58 S. a. Kucharski and R. J. Bartlett, *The Journal of Chemical Physics*, 1998, **108**, 9221–9226.

59 J. Cullen, *Chemical Physics*, 1996, **202**, 217–229.

60 T. Van Voorhis and M. Head-Gordon, *Chemical Physics Letters*, 2000, **317**, 575–580.

61 T. Van Voorhis and M. Head-Gordon, *The Journal of Chemical Physics*, 2001, **115**, 7814–7821.

62 P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck and P. Bultinck, *Journal of Chemical Theory and Computation*, 2013, **9**, 1394–1401.

63 T. Stein, T. M. Henderson and G. E. Scuseria, *The Journal of Chemical Physics*, 2014, **140**, 214113.

64 K. Boguslawski, *The Journal of Chemical Physics*, 2017, **147**, 139901.

65 F. Kossoski, A. Marie, A. Scemama, M. Caffarel and P.-F. Loos, *Journal of Chemical Theory and Computation*, 2021, **17**, 4756–4768.

66 M. Ravi, A. Perera, Y. C. Park and R. J. Bartlett, *The Journal of Chemical Physics*, 2023, **159**, 094101.

67 R. J. Bartlett and J. Noga, *Chemical Physics Letters*, 1988, **150**, 29–36.

68 Z. Windom, A. Perera and R. J. Bartlett, *The Journal of Chemical Physics*, unpublished, umpublished.

69 R. J. Bartlett, S. A. Kucharski and J. Noga, *Chemical Physics Letters*, 1989, **155**, 133–140.

70 J. D. Watts, G. W. Trucks and R. J. Bartlett, *Chemical physics letters*, 1989, **157**, 359–366.

71 L. Adamowicz and R. J. Bartlett, *Journal of Chemical Physics*, 1985, **83**, 6268.

72 J. Geertsen, M. Rittby and R. J. Bartlett, *Chemical Physics Letters*, 1989, **164**, 57–62.

73 J. F. Stanton and R. J. Bartlett, *The Journal of Chemical Physics*, 1993, **98**, 7029–7039.

74 D. C. Comeau and R. J. Bartlett, *Chemical Physics Letters*, 1993, **207**, 414–423.

75 P. B. Rozyczko and R. J. Bartlett, *The Journal of Chemical Physics*, 1998, **108**, 7988–7993.

76 T. J. Watson Jr, V. F. Lotrich, P. G. Szalay, A. Perera and R. J. Bartlett, *The Journal of Physical Chemistry A*, 2013, **117**, 2569–2579.

77 S. P. A. Sauer, M. Schreiber, M. R. Silva-Junior and W. Thiel, *Journal of Chemical Theory and Computation*, 2009, **5**, 555–564.

78 D. A. Matthews and J. F. Stanton, *The Journal of Chemical Physics*, 2016, **145**, 124102.

79 P.-F. Loos, M. Boggio-Pasqua, A. Scemama, M. Caffarel and D. Jacquemin, *Journal of Chemical Theory and Computation*, 2019, **15**, 1939–1956.

80 H. Koch, O. Christiansen, P. Jorgensen, A. M. Sanchez de Merás and T. Helgaker, *The Journal of Chemical Physics*, 1997, **106**, 1808–1818.

81 D. R. Nascimento and A. E. DePrince, *Journal of Chemical Theory and Computation*, 2016, **12**, 5834–5840.

82 D. R. Nascimento and A. E. DePrince, *The Journal of Physical Chemistry Letters*, 2017, **8**, 2951–2957.

83 Y. C. Park, A. Perera and R. J. Bartlett, *The Journal of Chemical Physics*, 2019, **151**, 164117.

84 Y. C. Park, A. Perera and R. J. Bartlett, *Journal of Chemical Physics*, 2021, **155**, 094103.

85 K. Ramasesha, S. R. Leone and D. M. Neumark, *Annual Review of Physical Chemistry*, 2016, **67**, 41–63.

86 R. J. Bartlett and D. S. Ranasinghe, *Chemical Physics Letters*, 2017, **669**, 54–70.

87 R. J. Bartlett, *The Journal of Chemical Physics*, 2019, **151**, 160901.

88 M. Nooijen and R. J. Bartlett, *The Journal of Chemical Physics*, 1997, **106**, 6449.

89 J. F. Stanton and J. Gauss, *Journal of Chemical Physics*, 1999, **111**, 8785–8788.

90 M. Musiał, A. Perera and R. J. Bartlett, *The Journal of Chemical Physics*, 2011, **134**, 114108.

91 M. Musiał, M. Olszówka, D. I. Lyakh and R. J. Bartlett, *The Journal of Chemical Physics*, 2012, **137**, 174102.

92 H. Koch, R. Kobayashi, A. Sanchez de Merás and P. Jo/rgensen, *The Journal of Chemical Physics*, 1994, **100**, 4393–4400.

93 M. Musiał and R. J. Bartlett, *The Journal of Chemical Physics*, 2011, **134**, 034106.

94 D. Mukherjee, *Pramana*, 1979, **12**, 203–225.

95 S. Pal, M. Rittby, R. J. Bartlett, D. Sinha and D. Mukherjee, *Chemical Physics Letters*, 1987, **137**, 273–278.

96 M. Nooijen and R. J. Bartlett, *The Journal of Chemical Physics*, 1997, **107**, 6812–6830.

97 L. S. Cederbaum and W. Domcke, *Theoretical Aspects of Ionization Potentials and Photoelectron Spectroscopy: A Green's Function Approach*, Advances in Chemical Physics 36, 2007, pp. 205–344.

98 J. V. Ortiz, *International Journal of Quantum Chemistry*, 1991, **40**, 35–42.

99 L. Meissner and R. J. Bartlett, *International Journal of Quantum Chemistry*, 1993, **48**, 67–80.

100 M. Nooijen and J. G. Snijders, *International Journal of Quantum Chemistry*, 1992, **44**, 55–83.

101 J. Oddershede, *Advances in Quantum Chemistry*, Academic Press, 1978, vol. 11, pp. 275–352.

102 D. Rowe, *Physics Letters B*, 1973, **44**, 155–158.

103 T. Korona, M. Przybytek and B. Jeziorski, *Molecular Physics*, 2006, **104**, 2303–2316.

104 T. Saue, R. Bast, A. S. P. Gomes, H. J. A. Jensen, L. Visscher, I. A. Aucar, R. Di Remigio, K. G. Dyall, E. Eliav, E. Fasshauer *et al.*, *The Journal of Chemical Physics*, 2020, **152**, 204104.

105 M. Reiher, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 139–149.

106 M. Barysz and A. J. Sadlej, *The Journal of Chemical Physics*, 2002, **116**, 2696–2704.

107 L. Cheng, Y. Xiao and W. Liu, *The Journal of Chemical Physics*, 2009, **131**, 244113.

108 J. Liu and L. Cheng, *WIREs Computational Molecular Science*, 2021, **11**, e1536.

109 A. Perera, Y. C. Park and R. J. Bartlett, *How Coupled-Cluster Theory is Solving the Electron Correlation Problem*, 2024, `https://www.sciencedirect.com/science/article/pii/B9780128219782001379`.

110 D. Bokhan, D. N. Trubnikov, A. Perera and R. J. Bartlett, *Chemical Physics Letters*, 2019, **730**, 372–377.

111 *Welcome to the NIST WebBook*, `https://webbook.nist.gov/`, (Accessed on 10/25/2023).

112 J. Q. Sun and R. J. Bartlett, *Journal of Chemical Physics*, 1996, **104**, 8553–8565.

113 J.-Q. Sun and R. J. Bartlett, *Physical Review Letters*, 1998, **80**, 349.

114 *Quantum Theory of Polymers: Proceedings of the NATO Advanced Study Institute on Electronic Structure and Properties of Polymers held at Namur, Belgium, 31 August - 4 September, 1977*, ed. J.-M. André, J. Delhalle and J. Ladik, Springer Science & Business Media, Nato Scien edn, 1977.

115 R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro and B. Kirtman, *WIREs Computational Molecular Science*, 2018, **8**, 1–36.

116 S. Hirata and S. Iwata, *The Journal of Chemical Physics*, 1998, **109**, 4147–4155.

117 S. Hirata, R. Podeszwa, M. Tobita and R. J. Bartlett, *The Journal of Chemical Physics*, 2004, **120**, 2581–2592.

118 M. Marsman, A. Grüneis, J. Paier and G. Kresse, *The Journal of Chemical Physics*, 2009, **130**, 184103.

119 A. Grüneis, M. Marsman and G. Kresse, *The Journal of Chemical Physics*, 2010, **133**, 074107.

120 A. Grüneis, G. H. Booth, M. Marsman, J. Spencer, A. Alavi and G. Kresse, *Journal of Chemical Theory and Computation*, 2011, **7**, 2780–2785.

121 M. F. Lange and T. C. Berkelbach, *The Journal of Chemical Physics*, 2021, **155**, 081101.

122 X. Wang and T. C. Berkelbach, *Journal of Chemical Theory and Computation*, 2020, **16**, 3095–3103.

123 X. Xing and L. Lin, *Journal of Chemical Theory and Computation*, 2022, **18**, 763–775.

124 F. Coester and H. Kümmel, *Nuclear Physics*, 1960, **17**, 477–485.

125 G. Hagen, T. Papenbrock, D. J. Dean and M. Hjorth-Jensen, *Physical Reviews C*, 2010, **82**, 034330.

126 G. Hagen, T. Papenbrock, A. Ekström, K. A. Wendt, G. Baardsen, S. Gandolfi, M. Hjorth-Jensen and C. J. Horowitz, *Physical Reviews C*, 2014, **89**, 014319.