

Correlations in Extended Systems: A Microscopic Multilocal Method for Describing Both Local and Global Properties

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Abstract

We review the basic principles of the various coupled cluster (CC) methods based on an exponential form for the many-body wavefunction, and contrast them with the configuration–interaction (CI) method. Particular emphasis is placed on their applicability to problems in quantum chemistry. We prove that in all cases we can construct an energy functional which variationally determines both the ground–state wavefunction and the dynamic equations of motion for nonstationary states. As a result the equations of motion assume the familiar classical canonical Hamiltonian form in some well-defined (multibody) configuration space. We also thereby construct the expectation-value functional for an arbitrary operator in such a way that the Feynman–Hellmann theorem is preserved at all natural levels of truncation of the appropriate configuration space. We show in detail that only in the case of the recently introduced extended CC method (ECCM) is the expectation-value functional expressed fully in terms of linked (multilocal) amplitudes. The ECCM is thereby capable of describing such global phenomena as shape transitions and other stereochemical properties, and the large-scale behavior of the molecular energy surfaces. We illustrate our methodology on the one-body density matrix, which is now much more easily discussed than by conventional methods in quantum chemistry.

Introduction

The coupled cluster method (CCM) is by now very well known in quantum chemistry and many areas of condensed matter physics as providing a very efficient fundamental formalism to include at the microscopic level the effects of quantum many-body correlations in both finite and extended systems. Recent reviews include those in Refs. [1–6].

The original (single-reference) version of the method was invented by Coester and Kümmel [7]. Based on the work of Hubbard [8], they introduced the characteristic exponential parametrization of the exact ground-state ket wavefunction $|\Psi_0\rangle$ of the interacting N -body system, $|\Psi_0\rangle = \exp(S)|\Phi\rangle$, in terms of a suitable reference state $|\Phi\rangle$, which for electronic-structure calculations, for example, is usually a Slater determinant of suitable single-particle orbitals (typically optimized

at the Hartree–Fock level). A key feature of the method is that the cluster operator S (which is usually denoted as T in the quantum chemistry literature, following the essentially independent reinvention of the method by Cizek [9]) may then be perturbatively decomposed wholly in terms of linked or connected terms. (We note that at this level of discussion the terms “linked” and “connected” in the context of diagrammatic perturbation theory, are synonymous.)

The ground-state Schrödinger equation, $H|\Psi_0\rangle = E_0|\Psi_0\rangle$, is then written in the typical CCM form,

$$e^{-S}He^S|\Phi\rangle = E_0|\Phi\rangle, \quad (1)$$

in which we see the very characteristic appearance of the similarity transformation that is another key feature of the CCM. The energy eigenvalue E_0 is readily obtained as

$$E_0 = \langle\Phi|e^{-S}He^S|\Phi\rangle, \quad (2)$$

where we have made use of the implied intermediate normalization $\langle\Phi|\Psi_0\rangle = 1$, employed henceforth. The microscopic CCM equations for the matrix elements of the cluster operator, S , are similarly obtained by taking the overlap of Eq. (1) with all remaining states that span the N -body Hilbert space. These are typically and conveniently chosen in electronic-structure calculations, for example, as the n -particle/ n -hole (np – nh) states ($n = 1, 2, \dots, N$) built on $|\Phi\rangle$ in terms of the same complete single-particle basis used to construct $|\Phi\rangle$ itself. By contrast with the more primitive configuration–interaction (CI) method [10], the CCM estimate for the energy so obtained is size-extensive even when the operator, S , is truncated. This is manifested by the fact that the expression in Eq. (2) for E_0 contains no unlinked terms, unlike its CI counterpart. Furthermore, the microscopic equations for the matrix elements of S contain no macroscopic terms that scale with particle number, N .

The great attraction of the similarity transformation $\hat{H} \equiv e^{-S}He^S$ in Eq. (1) is that, by using the fact that all partitions of S are composed of creation operators only with respect to the state $|\Phi\rangle$, we see that the well-known (and otherwise infinite) nested commutator expansion for \hat{H} terminates after a finite number of terms. For example, this occurs at the term involving four powers of S if H contains at most two-body operators, as is the case for Coulombic systems. By now applications of the method abound to a diversity of physical systems. Illustrative examples and some typical references include atoms and molecules [3,6,9,11–14], the homogeneous electron liquid [2,15–17], atomic nuclei and extended nuclear matter [1,4,18], anharmonic oscillators [19–21], and systems in relativistic quantum field theory [22]. In all of these cases, the quantitative results for the energies of the systems achieved by the CCM are at least as good as those achieved by any alternative microscopic method. Typical of the accuracy achievable is the case of the correlation energy for the electron gas, where over the entire density range of interest for real metals ($1 \lesssim r_s \lesssim 6$), the CCM results [15,16] are accurate to better than about 1% by comparison with the essentially exact results of Green function Monte Carlo

calculations [23]. In quantum chemistry the comparable goal of “chemical accuracy” has been to calculate correlation energies to better than about 1 mH. This goal has now essentially been achieved by the CCM for several molecules of interest [12–14]. We also note in passing that this standard of success in quantum chemistry has recently led to the hope [24] that comparable methods may be applied to problems in relativistic quantum chromodynamics (QCD) in order to achieve either higher accuracy than has proven possible with standard lattice Monte Carlo simulations, or comparable accuracy with much reduced computational effort.

In a typical quantum chemistry study involving molecules and their reactions, one may not only wish directly to calculate energies but also such other properties as energy gradients. Such calculations permit an efficient search of an energy surface in order both to locate such important features as minima and transition states for decomposition reactions, and to predict vibrational spectra. Other obvious properties of interest include, for example, spin–spin coupling constants and polarizability tensors. Now, the situation is less straightforward within the CCM for the calculation of observables or properties other than the energy. Thus, in order to calculate the expectation value \bar{A} of an arbitrary operator, A , for example, we need also to parametrize the bra state. The most straightforward way, employed independently by Čížek [9] and Fink [25], is to keep the bra and ket states manifestly hermitian-adjoint to each other, to give the expression

$$\bar{A} = \langle \Phi | e^{S^\dagger} A e^S | \Phi \rangle / \langle \Phi | e^{S^\dagger} e^S | \Phi \rangle \quad (3a)$$

$$= \langle \Phi | (e^{S^\dagger} A e^S)_{\mathcal{L}} | \Phi \rangle . \quad (3b)$$

Although Eq. (3a) may also be reduced to the sum in Eq. (3b) of linked (\mathcal{L}) diagrams [9,25], there is no such automatic termination upon expansion in powers of S as occurs in Eq. (2). Furthermore, when approximated by truncation, this method of calculation is in conflict with the important Feynman–Hellmann theorem, which implies that \bar{A} should be calculated diagrammatically from the same set of diagrams for the energy, but in which each interaction potential is replaced in turn by the operator A [26]. A more sophisticated method of calculating \bar{A} within the CCM due to Kümmel [27] is also in similar conflict with this theorem.

Monkhorst [28] gave the first formulation of \bar{A} within the CCM which is compatible with the Feynman–Hellmann theorem, by using techniques of linear (and higher-order) response theory, although he never introduced an explicit average-value functional. When supplemented by the introduction of basis set effects [29] that are essential for the practical analytic evaluation of energy derivatives in quantum chemistry, this scheme has rather successfully been used [30] to predict vibrational spectra and to locate transition states for decomposition reactions.

Finally, one of the present authors has shown [31] how to introduce two different explicit CCM parametrizations of the bra state which are not manifestly hermitian conjugate to the ket state, but which both (i) lead to explicit functionals for an arbitrary average value \bar{A} , (ii) give compatibility with the Feynman–Hellmann theorem, and (iii) are derivable from a variational principle. The first of these

corresponds to a generalization of the method of Monkhorst [28], and is nowadays referred to as the normal CCM (NCCM). It parametrizes the bra state $\langle \tilde{\Psi}_0 |$ (with $\langle \tilde{\Psi}_0 | \Psi_0 \rangle = 1$) in the form

$$\begin{aligned} \langle \tilde{\Psi}_0 | &= \langle \Phi | \tilde{\Omega} e^{-S}, \\ \langle \Phi | \tilde{\Omega} &= \frac{\langle \Phi | e^{S^\dagger} e^S}{\langle \Phi | e^{S^\dagger} e^S | \Phi \rangle}. \end{aligned} \quad (4)$$

For the ground state, although $\bar{A} = \langle \Phi | \tilde{\Omega} e^{-S} A e^S | \Phi \rangle$ is generally composed wholly of linked terms, it was shown that the operator $\tilde{\Omega}$ (composed wholly in terms of destruction operators with respect to $|\Phi\rangle$) contains unlinked terms.

On the other hand, it was also shown that $\tilde{\Omega}$ could itself be written in exponential form, $\tilde{\Omega} = \exp(\tilde{\Sigma})$, in terms of a new (destruction) operator $\tilde{\Sigma}$ which contains only linked terms. The corresponding complete parametrization of \bar{A} in terms of the operators S and $\tilde{\Sigma}$ is nowadays referred to as the extended CCM (ECCM). Quantum chemists should beware however that this same terminology is sometimes used to indicate a truncated NCCM calculation which goes beyond the CCSD approximation (which includes singles and doubles only in terms of the n -body partitions of S corresponding to np - nh excitations from $|\Phi\rangle$) or, equivalently, the SUB(2) level.

One of the key distinguishing features of the ECCM which follows from its double exponential structure, is that by contrast with the NCCM and the CI method *all* of the basic amplitudes (which represent the matrix elements of the operators S and $\tilde{\Sigma}$) that completely characterize the system are linked-cluster quantities with well-defined diagrammatic representations. In turn they all thus obey the cluster property, namely that they become zero as any subset of particles described by the amplitude becomes far removed from the remainder. The entire system may thus be parametrized in terms of a complete set of ECCM multilocal classical (i.e., c -number) amplitudes. We have shown elsewhere [32] how an arbitrary quantum-mechanical problem with underlying Schrödinger dynamics may be exactly mapped onto a classical field theory in which the ECCM amplitudes interact via nonlocal classical interactions. We have further shown [33] how these amplitudes may also be viewed as generalized many-body mean fields or quasilocal order parameters, by considering their small-amplitude dynamics around a stationary equilibrium point.

Successful applications of the ECCM to date include the quantum fluid dynamics of a zero-temperature condensed Bose fluid [34], the problem of a charged impurity in a polarizable medium (of relevance to the important experimental tool of positron annihilation in metals, alloys, and other condensed matter systems) [35], and anharmonic oscillators and spin systems [36]. Since virtually all of the very successful quantum chemistry CCM calculations to date have used the NCCM, one of our main aims here is to highlight the additional attractive features possessed by the ECCM which we hope may be of value for future applications in this field.

Thus, we shall indicate how in its general dynamical formulation the ECCM is capable of describing both equilibrium and nonequilibrium behavior, as well as such intrinsically nonperturbative aspects of many-body systems as spontaneous

symmetry breaking, phase transitions, and states of topological excitation or deformation. It thus has the ability to describe simultaneously both local and global properties of the system. The latter would include for molecules, for example, both the stereochemical structure in real space, and the topology of the potential energy surfaces.

In the next section we compare the CI, NCCM, and ECCM parametrizations at the most general level of their respective descriptions for a time-dependent state of a many-body system. We first show how each of them can be cast variationally from a stationary principle for the action functional, in terms of a canonical set of dynamical equations of motion of similar generic form. We then indicate in the subsequent section, by specializing to the equilibrium ground state, how the three methods differ in their incorporation of the locality and separability features discussed above, which are so important for extended systems. Our findings are summarized in the last section, and we compare the schemes presented here with other alternative coupled cluster (CC) schemes for evaluating expectation values of arbitrary operators.

CI and CC Dynamical Descriptions

In a typical quantum chemistry calculation, the Hamiltonian is written in the occupation number representation as,

$$H = \sum_{i,j} f_{ij} a_i^\dagger a_j + \frac{1}{4} \sum_{i,j,k,l} \langle ij || kl \rangle a_i^\dagger a_j^\dagger a_l a_k \equiv f + W, \quad (5)$$

where f_{ij} is a Fock matrix element and $\langle ij || kl \rangle$ is an antisymmetrized two-electron integral, relative to a complete set of (orthonormal) molecular (spin-) orbitals defined in terms of the vacuum state $|\text{vac}\rangle$ and the corresponding creation and destruction operators a_i^\dagger and a_j which satisfy the usual fermionic anticommutation relations. For the usual Hartree-Fock or self-consistent field (SCF) case the one-body operator f is diagonal,

$$f = \sum_i \epsilon_i a_i^\dagger a_i. \quad (6)$$

A typical (normalized) N -body reference state $|\Phi\rangle$ is then the usual Slater determinant formed from the N states $\{a_\alpha^\dagger |\text{vac}\rangle; \alpha = 1, 2, \dots, N\}$ of lowest energy ϵ_α ,

$$|\Phi\rangle = \prod_{\alpha=1}^N a_\alpha^\dagger |\text{vac}\rangle; \quad \langle \Phi | \Phi \rangle = 1. \quad (7)$$

Henceforth we use the convention that indices $\{\alpha, \beta, \dots\}$ label the hole states that can be created by removing a particle in $|\Phi\rangle$, indices $\{p, q, \dots\}$ label the remaining unoccupied or particle states, and indices $\{i, j, \dots\}$ label a general (particle or hole) state.

We now introduce general creation operators X and destruction operators \tilde{Y} with respect to the reference state $|\Phi\rangle$. Both contain m -particle/ m -hole partitions with respect to $|\Phi\rangle$, with $m = 1, 2, \dots, N$,

$$X = \sum_m X_m; \quad \tilde{Y} = \sum_m \tilde{Y}_m,$$

$$X_m = \frac{1}{(m!)^2} \sum_{p_1 \dots p_m} \sum_{\alpha_1 \dots \alpha_m} \langle p_1 \dots p_m | X_m | \alpha_1 \dots \alpha_m \rangle_A a_{p_1}^\dagger \dots a_{p_m}^\dagger a_{\alpha_m} \dots a_{\alpha_1},$$

$$\tilde{Y}_m = \frac{1}{(m!)^2} \sum_{p_1 \dots p_m} \sum_{\alpha_1 \dots \alpha_m} \langle \alpha_1 \dots \alpha_m | \tilde{Y}_m | p_1 \dots p_m \rangle_A a_{\alpha_1}^\dagger \dots a_{\alpha_m}^\dagger a_{p_m} \dots a_{p_1},$$

(8)

where the suffix, A , indicates an antisymmetrized matrix element. Alternatively, in terms of a configuration index I which represents the *set* of single-particle indices $\{p_1 \dots p_m, \alpha_1 \dots \alpha_m\}$, we write in an obvious notation,

$$X = \sum'_I x_I C_I^\dagger, \quad \tilde{Y} = \sum'_I \tilde{y}_I C_I, \quad (9)$$

$$C_I^\dagger = a_{p_1}^\dagger \dots a_{p_m}^\dagger a_{\alpha_m} \dots a_{\alpha_1}, \quad I = \{p_1 \dots p_m, \alpha_1 \dots \alpha_m\}, \quad (10)$$

and the sums on I in Eq. (9) run over all possible m -particle/ m -hole configurations with respect to $|\Phi\rangle$, for $m = 1, 2, \dots, N$. We use the convention that the prime on the summations in Eq. (9) indicate that we omit the ($m = 0$ or) $I = 0$ configuration of $|\Phi\rangle$ itself, where $C_0^\dagger = C_0 \equiv \mathbb{1}$, the identity operator. Alternatively, if we omit the prime from a sum on I , we include this $I = 0$ configuration. Thus, for example,

$$\sum_I C_I^\dagger |\Phi\rangle \langle \Phi | C_I = \mathbb{1} = |\Phi\rangle \langle \Phi | + \sum'_I C_I^\dagger |\Phi\rangle \langle \Phi | C_I. \quad (11)$$

We denote the two sets of all such creation operators X and all such destruction operators \tilde{Y} as \mathcal{C} and $\tilde{\mathcal{C}}$ respectively. Both sets include the identity.

The time-dependent Schrödinger equations for exact ket states $|\Psi\rangle = |\Psi(t)\rangle$ and bra states $\langle \tilde{\Psi} | = \langle \tilde{\Psi}(t) |$ are

$$H|\Psi\rangle = i \frac{\partial}{\partial t} |\Psi\rangle; \quad \langle \tilde{\Psi} | H = -i \frac{\partial}{\partial t} \langle \tilde{\Psi} |. \quad (12)$$

We choose the normalization such that $\langle \tilde{\Psi} | \Psi \rangle = 1$ for all times, t . Thus, when the Hamiltonian is hermitian (as usual), $H = H^\dagger$, we have $\langle \tilde{\Psi} | = \langle \Psi | \Psi \rangle^{-1} \times \langle \Psi |$, where $\langle \Psi | = (|\Psi\rangle)^\dagger$. It is important to realize from the outset that it is not vital to preserve the hermitian conjugacy of $|\Psi\rangle$ and $\langle \tilde{\Psi} |$ at a given level of approximation, as we shall see below. In terms of the action functional,

$$\mathcal{A} \equiv \int_{t_1}^{t_2} dt \langle \tilde{\Psi}(t) | \left(i \frac{\partial}{\partial t} - H \right) | \Psi(t) \rangle, \quad (13)$$

Eqs. (12) are completely equivalent to the stationarity principle,

$$\delta \mathcal{A} / \delta \langle \tilde{\Psi} | = 0 = \delta \mathcal{A} / \delta | \Psi \rangle, \quad (14)$$

for all independent variations in the bra and ket states such that $|\delta \Psi(t_k)\rangle = 0 = \langle \delta \tilde{\Psi}(t_k) |$; $k = 1, 2$.

Different parametrizations of the bra and ket states now lead to different implementations of the stationarity principle. The most straightforward is the CI scheme,

$$\begin{aligned} |\Psi\rangle &= F|\Phi\rangle; & \langle \tilde{\Psi} | &= \langle \Phi | \tilde{F}, \\ F &= \sum_I f_I C_I^\dagger; & \tilde{F} &= \sum_I \tilde{f}_I C_I, \end{aligned} \quad (15)$$

from which it is trivial to show that Eq. (14) leads to the canonical equations of motion,

$$i \frac{df_I}{dt} = \frac{\partial \bar{H}}{\partial \tilde{f}_I}; \quad -i \frac{d\tilde{f}_I}{dt} = \frac{\partial \bar{H}}{\partial f_I}, \quad (16)$$

where $\bar{H} \equiv \langle \tilde{\Psi}(t) | H | \Psi(t) \rangle = \bar{H}[f_I, \tilde{f}_I; t]$. Equations (16) are exact when the configuration space is not truncated, and otherwise lead to the standard CI equations if the indices I are truncated. A typical SUB(n) approximation limits the configurations I to those defined in Eq. (10) with $m \leq n$. For example, SUB(3) approximation keeps only the $m = 1$ (singles), $m = 2$ (doubles), and $m = 3$ (triples) configurations, to give what is more usually called the CISDT approximation in the quantum chemistry literature.

In the NCCM the ket state is written in the usual form,

$$|\Psi\rangle = k e^S |\Phi\rangle; \quad S = \sum_I' s_I C_I^\dagger, \quad (17)$$

where $k = k(t)$ is a (c -number) time-dependent scale factor. We may now ask whether it is possible to parametrize the bra state $\langle \tilde{\Psi} |$ in a form which is not manifestly hermitian conjugate to $|\Psi\rangle$ but so that the canonical form of the equations of motion,

$$i \frac{dx_I}{dt} = \frac{\partial \bar{H}}{\partial \tilde{y}_I}; \quad -i \frac{d\tilde{y}_I}{dt} = \frac{\partial \bar{H}}{\partial x_I}, \quad (18)$$

is preserved when $\{x_I\} \rightarrow \{s_I\}$. In other words, we now seek a NCCM parametrization of $\langle \tilde{\Psi} |$ in terms of a destruction operator $\tilde{Y} \in \tilde{\mathcal{C}}$ with amplitudes $\{\tilde{y}_I\}$ as in Eq. (9) canonically conjugate to the creation cluster amplitudes $\{s_I\}$. It is easily seen that this is readily achieved by writing $\{\tilde{y}_I\} \rightarrow \{\tilde{\omega}_I\}$, where

$$\langle \tilde{\Psi} | = \frac{1}{k} \langle \Phi | \tilde{\Omega} e^{-S}; \quad \tilde{\Omega} = 1 + \sum_I' \tilde{\omega}_I C_I. \quad (19)$$

The NCCM thus fully parametrizes the system in terms of amplitudes $\{x_I \rightarrow s_I, \tilde{y}_I \rightarrow \tilde{\omega}_I\}$. It has the great advantage over the CI method, where $\{x_i \rightarrow f_i, \tilde{y}_I \rightarrow \tilde{f}_I\}$, that an arbitrary average-value functional, $\bar{A} \equiv \langle \tilde{\Psi}(t) | A | \Psi(t) \rangle = \bar{A}[x_I, \tilde{y}_I; t]$ is composed of fully linked terms only.

Just as considerable advantages have accrued from writing the CI wave operator F in the linked-cluster exponential form $F \equiv \exp(S)$, so it is now similarly advantageous to write $\tilde{\Omega}$ in what also turns out to be a linked-cluster form,

$$\tilde{\Omega} \equiv \exp(\tilde{\Sigma}); \quad \tilde{\Sigma} = \sum_I' \tilde{\sigma}_I C_I, \quad (20)$$

which defines the ECCM parametrization. Although the ECCM may thus be fully specified in terms of the amplitudes $\{s_I, \tilde{\sigma}_I\}$, these do not form a canonically conjugate set in the sense of satisfying Eq. (18). Indeed, if we wish to keep the canonical form of Eq. (18) with $\{\tilde{y}_I\} \rightarrow \{\tilde{\sigma}_I\}$, it is simple to see that the corresponding parametrization of the ket vector must be given in terms of a new creation operator $\Sigma \in \mathcal{C}$, where

$$\Sigma |\Phi\rangle \equiv Q e^{\tilde{\Sigma}} S |\Phi\rangle; \quad \Sigma = \sum_I' \sigma_I C_I^\dagger, \quad (21)$$

where $Q \equiv \mathbb{1} - |\Phi\rangle\langle\Phi|$ is the projector into the complementary space of the model reference state. Then the ECCM set of amplitudes $\{x_I \rightarrow \sigma_I, \tilde{y}_I \rightarrow \tilde{\sigma}_I\}$ also satisfies the canonical equations of motion (18). Equation (21) has the inverse transformations

$$s_I = \langle \Phi | C_I e^{\tilde{\Sigma}} S | \Phi \rangle, \quad \sigma_I = \langle \Phi | C_I e^{-\tilde{\Sigma}} \Sigma | \Phi \rangle. \quad (22)$$

Either of the sets $\{s_I, \tilde{\sigma}_I\}$ and $\{\sigma_I, \tilde{\sigma}_I\}$ is thus complete and sufficient to specify the ECCM.

We have thus seen how each of the three methods, namely (i) the CI method, (ii) the NCCM, and (iii) the ECCM, satisfies the dynamical equations of motion in the same generic canonical form of Eq. (18). The canonically conjugate basic operators $\{X, \tilde{Y}\}$ are respectively (i) $\{F, \tilde{F}\}$, (ii) $\{S, \tilde{\Omega}\}$, (iii) $\{\Sigma, \tilde{\Sigma}\}$. Although the corresponding classical phase spaces, parametrized and spanned by the respective configuration-space (c -number) amplitudes $\{x_I, \tilde{y}_I\}$, are in principle all equally complicated, the three individual forms of the Hamiltonian functional $\bar{H}[x_I, \tilde{y}_I; t]$ lead to distinct differences. These are specifically reflected in the respective locality and separability features of the three methods. Just as the NCCM has the well-known advantages in this regard over the CI method when we consider only the ground-state energy functional $E_0 = E_0[s_I]$ of Eq. (2), so we shall see below that when considering an arbitrary expectation-value functional \bar{A} , and hence when we need to consider *both* sets of amplitudes $\{x_I\}$ and $\{\tilde{y}_I\}$, the ECCM has comparable advantages over the NCCM. We also note that all three methods can be systematically approximated in terms of a SUB(n) truncation scheme for the respective canonical parameters $\{x_I, \tilde{y}_I\}$, in which only n -tuply excited configurations described by the indices I are included in the sums on I . This results in finite expressions for the energy in each case.

Stationary Ground-State Descriptions and Diagrammatics

We first remark that from Eqs. (17) and (19) we see that the NCCM amplitudes $\{\tilde{\omega}_I\}$ are just given by the average values of the corresponding creation operators, $\tilde{\omega}_I = \langle C_I^\dagger \rangle$, and hence it is clear that these are not linked quantities. Conversely, the definition in Eq. (20) shows that the linked (\mathcal{L}) parts of these averages are precisely the corresponding ECCM amplitudes, $\tilde{\sigma}_I = \langle C_I^\dagger \rangle_{\mathcal{L}}$. Furthermore, it is clear from the definition in Eq. (22) that the remaining ECCM amplitudes $\{\sigma_I\}$ are also linked provided that the NCCM amplitudes $\{s_I\}$ are. As is well known, the fact that Hubbard [8] has shown that the operator S for the exact ground state $|\Psi_0\rangle$ is just such a sum of linked diagrams, lies at the heart of the entire CC methodology.

In order to make further contact with the diagrammatic expansions of many-body perturbation theory (MBPT), it is convenient to specialize the above dynamical treatment to the stationary (in time) equilibrium values of the various parametrizations $\{x_I, \tilde{y}_I\}$ that characterize the exact ground-state eigenvalues $|\Psi_0\rangle$ and $\langle \tilde{\Psi}_0|$. In this case the generic variational equations (18) become simply the stationarity conditions, $\partial \bar{H} / \partial \tilde{y}_I = 0 = \partial \bar{H} / \partial x_I$, for the energy expectation value. For the NCCM, where $\bar{H} = \langle \Phi | \tilde{\Omega} e^{-S} H e^S | \Phi \rangle$ and $x_I \rightarrow s_I$, $\tilde{y}_I \rightarrow \tilde{\omega}_I$, these equations trivially become

$$\langle \Phi | C_I e^{-S} H e^S | \Phi \rangle = 0; \quad I \neq 0, \quad (23)$$

$$\langle \Phi | \tilde{\Omega} e^{-S} [H, C_I^\dagger] e^S | \Phi \rangle = 0; \quad I \neq 0. \quad (24)$$

Equation (23) is just the usual coupled set of (finite-order) CCM equations for the amplitudes s_I , and Eq. (24) is its counterpart for the amplitudes $\tilde{\omega}_I$. By making use of Eq. (11) it is clear that Eq. (23) is equivalent to the Schrödinger Eqs. (1) and (2) for the ground ket state. Furthermore, Eqs. (24) and (23) together similarly lead to the comparable bra-state equation,

$$\langle \Phi | \tilde{\Omega} e^{-S} (H - E_0) e^S = 0. \quad (25)$$

In the practical schemes to utilize the NCCM or the ECCM, we now typically solve Eqs. (23) and (24) with the corresponding amplitudes restricted to the SUB(n) truncation scheme. In such cases the restricted ket vectors $\exp(S)|\Phi\rangle$ and bra vectors $\langle \Phi | \tilde{\Omega} \exp(-S)$ and $\langle \Phi | \exp(\tilde{S}) \exp(-S)$ do not fully span the entire Hilbert space, and the corresponding variational calculations are only approximate. We further note that although both CCM calculations are variational, they do *not* necessarily give upper bounds for the energy eigenvalue E_0 in SUB(n) approximations. Thus, the quantity $\langle \tilde{\Psi} | (H - E_0) | \Psi \rangle / \langle \tilde{\Psi} | \Psi \rangle$ is only manifestly positive-semidefinite for all wavefunctions $|\Psi\rangle$ and $\langle \tilde{\Psi} |$ when $\langle \tilde{\Psi} | \propto (|\Psi\rangle)^\dagger$, as in the CI method, but not in either the NCCM or the ECCM.

Our methods so far have been to treat the amplitudes $\{x_I, \tilde{y}_I\}$ as variable parameters to be determined by a variational principle. These methods and the truncation schemes are quite self-contained and fully prescribed. Nevertheless it is useful to make contact with the diagrammatic expansions of MBPT. In order to do this we now restrict ourselves to the canonical SCF case where the one-body term f in the

Hamiltonian is diagonal and given by Eq. (6). It is then easy to evaluate explicitly the term $\bar{f} \equiv \langle \tilde{\Psi}_0 | f | \Psi_0 \rangle$ from the energy expectation value, $\bar{H} = \bar{f} + \bar{W}$, in each of the three representations, since in this case the complete set of states $|\Phi\rangle$ and $C_I^\dagger |\Phi\rangle$ are eigenstates of f ,

$$\begin{aligned} f|\Phi\rangle &= \mathcal{E}_0|\Phi\rangle; & \mathcal{E}_0 &= \sum_{\alpha=1}^N \varepsilon_\alpha, \\ fC_I^\dagger|\Phi\rangle &= (\mathcal{E}_0 + e_I)C_I^\dagger|\Phi\rangle, \\ e_I &\equiv \sum_{i=1}^m (\varepsilon_{p_i} - \varepsilon_{\alpha_i}); & I &= \{p_1 \cdots p_m, \alpha_1 \cdots \alpha_m\}. \end{aligned} \quad (26)$$

In the CI representation it is then trivial to see that

$$\bar{f} = \langle \Phi | \tilde{F} f F | \Phi \rangle = \mathcal{E}_0 + \langle \Phi | \tilde{F} (f - \mathcal{E}_0) F | \Phi \rangle = \mathcal{E}_0 + \sum_I' e_I \tilde{f}_I f_I, \quad (27)$$

by an obvious insertion of the complete set of states of Eq. (11). Furthermore, since each term in Eq. (6) contains exactly one creation operator with respect to $|\Phi\rangle$, namely a_p^\dagger or a_α , and since S similarly contains only such creation operators, we have

$$e^{-S} f e^S = f + [f, S], \quad (28)$$

where the higher-order terms in the nested commutator expansion vanish identically. We then similarly find that the NCCM expansion for \bar{f} is

$$\bar{f} = \langle \Phi | \tilde{\Omega} e^{-S} f e^S | \Phi \rangle = \mathcal{E}_0 + \langle \Phi | \tilde{\Omega} (f - \mathcal{E}_0) S | \Phi \rangle = \mathcal{E}_0 + \sum_I' e_I \tilde{\omega}_I s_I. \quad (29)$$

Finally, the ECCM expression is obtained by replacing $\tilde{\Omega} \rightarrow \exp(\tilde{\Sigma})$, to get

$$\bar{f} = \mathcal{E}_0 + \langle \Phi | e^{\tilde{\Sigma}} (f - \mathcal{E}_0) e^{-\tilde{\Sigma}} e^{\tilde{\Sigma}} S | \Phi \rangle. \quad (30)$$

A similar expansion to that in Eq. (28) for the similarity transform in Eq. (30), then leads to the expression

$$\bar{f} = \mathcal{E}_0 + \langle \Phi | \tilde{\Sigma} (f - \mathcal{E}_0) \Sigma | \Phi \rangle = \mathcal{E}_0 + \sum_I' e_I \tilde{\sigma}_I \sigma_I, \quad (31)$$

where we have used the definition of Σ in Eq. (21).

We thus see from Eqs. (27), (29), and (31) that each of our three representations has the same generic form for the energy expectation value,

$$\bar{H} = \bar{H}[x_I, \tilde{y}_I] = \mathcal{E}_0 + \sum_I' e_I x_I \tilde{y}_I + \bar{W}[x_I, \tilde{y}_I], \quad (32)$$

and they differ only in their explicit form for the potential energy average-value functional \bar{W} . The stationarity principle therefore leads in each case to the generic Dyson equations for the amplitudes,

$$\tilde{y}_I = -\frac{1}{e_I} \frac{\partial \bar{W}}{\partial x_I}; \quad x_I = -\frac{1}{e_I} \frac{\partial \bar{W}}{\partial \tilde{y}_I}. \quad (33)$$

We now see the factors e_I appearing in the familiar guise of energy denominators. The iterative solutions of Eq. (33) lead to sets of terms which can rather obviously be placed in a one-to-one correspondence with classes of MBPT (Goldstone) diagrams.

The CI functional $\bar{W} = \bar{W}[f_I, \tilde{f}_I]$,

$$\bar{W} = \sum_{I,J} W_{IJ} \tilde{f}_I f_J; \quad W_{IJ} \equiv \langle \Phi | C_I W C_J^\dagger | \Phi \rangle, \quad (34)$$

has the great merit of simplicity but clearly suffers from the well-known inclusion of disconnected terms and the consequent lack of size-extensivity. Equations (33) and (34) lead to the usual sets of linear CI equations,

$$e_I f_I + \sum_J W_{IJ} f_J = 0; \quad e_I \tilde{f}_I + \sum_J \tilde{f}_J W_{JI} = 0, \quad (35)$$

from which it is clear that both sets of amplitudes $\{f_I\}$ and $\{\tilde{f}_I\}$ contain disconnected terms.

By contrast, the NCCM functional $\bar{W} = \bar{W}[s_I, \tilde{\omega}_I]$ is fully connected,

$$\bar{W}[s_I, \tilde{\omega}_I] = \langle \Phi | \tilde{\Omega} e^{-S} W e^S | \Phi \rangle = \sum_{n=0}^4 \frac{1}{n!} \langle \Phi | \tilde{\Omega} (W S^n)_{\mathcal{L}} | \Phi \rangle, \quad (36)$$

where the linking (\mathcal{L}) now comes from the nested-commutator expansion. Whereas the amplitudes $\{s_I\}$, now given by Eqs. (33) and (36) as solutions to the usual nonlinear coupled CCM equations,

$$s_I = -\frac{1}{e_I} \sum_{n=0}^4 \frac{1}{n!} \langle \Phi | C_I (W S^n)_{\mathcal{L}} | \Phi \rangle, \quad (37)$$

are self-evidently linked, the amplitudes $\{\tilde{\omega}_I\}$ still contain unlinked terms.

Finally, the ECCM functional $\bar{W} = \bar{W}[\sigma_I, \tilde{\sigma}_I]$ is obtained from Eq. (36) by the replacement $\tilde{\Omega} \rightarrow \exp(\tilde{\Sigma})$. By a rather straightforward expansion of the resulting expression into diagrams, and by using the definition of Eqs. (21) and (22), it is not difficult to see that $\bar{W}[\sigma_I, \tilde{\sigma}_I]$ now has an even more connected form, which can be written formally as

$$\bar{W}[\sigma_I, \tilde{\sigma}_I] = \sum_{n=0}^4 \frac{1}{n!} \langle \Phi | e^{\tilde{\Sigma}} (W \Sigma^n)_{\mathcal{L}} | \Phi \rangle_{\mathcal{DL}}, \quad (38)$$

where, as before, the linking (\mathcal{L}) constraint requires that each σ -amplitude must be connected (by at least one particle or hole line) to the interaction operator W ; and the double-linking (\mathcal{DL}) constraint requires that if a $\tilde{\sigma}$ -amplitude is not also similarly connected directly to W , it must be connected to at least two different σ -

amplitudes. It is then easy to see that this extra connectivity of \bar{W} ensures that *all* ECCM amplitudes $\{\sigma_I, \tilde{\sigma}_I\}$ are fully connected. It is this basic property which ensures that at all SUB(n) levels of approximation within the ECCM: (i) the size-extensivity and size-consistency properties are obeyed, (ii) both the bra and ket wavefunctions are properly (multiplicatively) separable in the dissociation limit, and (iii) all of the basic amplitudes $\{\sigma_I, \tilde{\sigma}_I\}$ exactly obey the cluster property. It is this latter property which in particular distinguishes the ECCM from both the NCCM and the CI method, and which makes the ECCM alone capable, at least in principle, of describing global properties of a system as well as the local properties which are so well handled by the NCCM.

We remark finally that the NCCM linking (\mathcal{L}) properties encapsulated in Eq. (36) are rooted ultimately in the single similarity transformation induced by the operator $\exp(S)$, and the ECCM double-linking (\mathcal{DL}) properties encapsulated in Eq. (38) are comparably rooted in the double similarity transformation induced by the two operators $\exp(S)$ and $\exp(\tilde{S})$. The structure of the corresponding diagrammatic expansions for \bar{W} can be further analyzed in terms of generalized tree diagrams with specific generalized time-ordering (GTO) properties [37]. The NCCM has well-known GTO properties “backwards in time” corresponding to the linked nature of the creation amplitudes $\{s_I\}$. The GTO property is a useful device for classifying and combining certain classes of Goldstone MBPT diagrams. It is based on the property of Goldstone diagrams containing disjoint sets of particle and hole lines, which permits a factorization of the corresponding energy denominators across such sets of lines after all time orderings are combined which preserve their particle or hole nature. The linked nature of both sets of amplitudes $\{\sigma_I\}$ and $\{\tilde{\sigma}_I\}$ in the ECCM similarly leads to this method being diagrammatically decomposable in terms of generalized tree diagrams which have the GTO property both forwards and backwards in time. The interested reader is referred to the literature [31,38] for further details.

Discussion

We first recall that due to their derivation from a stationarity principle, both versions of the CCM presented here share with the CI method that they satisfy the Feynman–Hellmann theorem. Thus, if when H undergoes a perturbation $H \rightarrow H + \delta H$, the corresponding wavefunctions undergo first-order changes $|\Psi\rangle \rightarrow |\Psi\rangle + |\delta\Psi\rangle$ and $\langle\tilde{\Psi}| \rightarrow \langle\tilde{\Psi}| + \langle\delta\tilde{\Psi}|$ so that the normalization $\langle\tilde{\Psi}|\Psi\rangle = 1$ is maintained, then

$$\delta\bar{H} = \langle\tilde{\Psi}|\delta H|\Psi\rangle. \quad (39)$$

Equation (39), true for the exact wavefunction, is thus shared by each of the CI, NCCM, and ECCM schemes in SUB(n) approximation. It ensures that the expectation value of an operator and the energy derivative of a Hamiltonian perturbed by that operator are equivalent. This is of particular importance in quantum chemistry since it provides a simple alternative method for calculating such properties as

gradients (which may derive, for example, from nuclear displacements or external fields) or moments. Furthermore, the satisfaction of the Feynman–Hellmann theorem ensures the usual “ $(2n + 1)$ rule” of perturbation theory, namely that a knowledge of the perturbed energy eigenfunction to n th order leads to a value for the perturbed energy eigenvalue to $(2n + 1)$ th order. Thus, a knowledge of the first-order perturbed amplitudes $\{\delta x_I, \delta y_I\}$ suffices to evaluate second and third energy derivatives,

$$\begin{aligned} \delta^2 \bar{H} &= \langle \tilde{\Psi} | \delta^2 H | \Psi \rangle + \langle \delta \tilde{\Psi} | \delta H | \Psi \rangle + \langle \tilde{\Psi} | \delta H | \delta \Psi \rangle, \\ \delta^3 \bar{H} &= \langle \tilde{\Psi} | \delta^3 H | \Psi \rangle + 3 \langle \delta \tilde{\Psi} | \delta^2 H | \Psi \rangle + 3 \langle \tilde{\Psi} | \delta^2 H | \delta \Psi \rangle \\ &\quad + 6 \langle \delta \tilde{\Psi} | (\delta H - \delta \bar{H}) | \delta \Psi \rangle, \end{aligned} \quad (40)$$

which can be used for such properties as force constants, magnetic susceptibility tensors, and the hyperpolarizabilities of interest for nonlinear optical behavior.

The rather small price that has been paid in these CC methods is the doubling of the number of independently determined amplitudes, which has arisen from giving up the explicit adjoint symmetry between the bra and ket states. This lack of manifest adjoint symmetry in the NCCM and ECCM also loses us the variational upper bound on the energy which the CI method retains. We see clearly that one must generally choose between maintaining the bound and maintaining the size-extensivity property. However, since only energy differences are physically observable in quantum chemistry, the loss of the bound for absolute energies is no real loss in practice.

The NCCM considered here may be compared with the alternative CCM technique for observables of Lührmann [39]. His method is identical to ours except for the construction of the $\{\tilde{\omega}_I\}$ amplitudes. While his $\{s_I\}$ amplitudes are calculated as in our Eq. (23), he chooses to calculate the set $\{\tilde{\omega}_I\}$ not from Eq. (24) but by preserving the exact adjoint relation $\langle C_I^\dagger \rangle = \langle C_I \rangle^*$ in SUB(n) approximation, so that

$$\tilde{\omega}_I = \langle \Phi | \tilde{\Omega} e^{-S} C_I e^S | \Phi \rangle^* \quad (41)$$

in his method. It is easy to see that this method does not preserve the Feynman–Hellmann theorem.

Finally, two other CC methods for calculating average values, which Bartlett refers to as the XCC (expectation-value CC) [9,25,40,41] and UCC (unitary CC) methods [41,42], have been discussed recently within quantum chemistry. The XCC method is based on Eq. (3), while the UCC method is based on a unitary ansatz [42],

$$\bar{A} = \langle \Phi | e^{\tau^\dagger} A e^\tau | \Phi \rangle = \sum_n \frac{1}{n!} \langle \Phi | (A \tau^n)_L | \Phi \rangle, \quad (42)$$

where $\tau \equiv S - S^\dagger = -\tau^\dagger$. Unlike the NCCM and ECCM expansions for \bar{A} , both the XCC and UCC expressions in Eqs. (3) and (42) lead to an infinite series of terms, even in SUB(n) approximation, rather than terminating into a closed form. However,

they may still be approximately implemented by further truncating, for example, so that the energy is correct to some given order in W in MBPT. The upper bound for the energy is thereby lost by both methods, even though they do preserve the explicit adjoint symmetry. The UCC method in this perturbative n th order truncation scheme does however preserve the (generalized) Feynman–Hellmann theorem, whereas the XCC method does not [41].

It seems clear from our discussion that both the NCCM and ECCM presented here are intrinsically more powerful, more systematic, and more consistent than any of these alternative techniques. It is our hope and expectation that the ECCM in particular will find rich applications in quantum chemistry both for the practical analytic evaluation of such local properties as the energy derivatives of great current interest, as well as for more global properties. We presume that these latter, which include topological excitations and phase or shape transitions, will become of increasing interest as the molecules under scrutiny become more complex, or as the studies are broadened to include such extended systems as polymers and solids.

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