Excitonic Coupled-cluster Theory:
Part I, General Formalism

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Abstract

One shortcoming of presently available fragment-based methods is that electron correlation (if included) is described at the level of individual electrons, resulting in many redundant evaluations of the electronic relaxations associated with any given fluctuation. A generalized variant of coupled-cluster (CC) theory is described here, wherein the degrees of freedom are fluctuations of fragments between internally correlated states. The effects of intra-fragment correlation on the inter-fragment interaction are pre-computed and permanently folded into an effective Hamiltonian. This article provides a high-level description of the CC variant, establishing some useful notation, and demonstrating the advantage of the proposed paradigm numerically on model systems. A companion article shows that the electronic Hamiltonian of real systems may always be cast in the form required. This framework opens a promising path to build finely tunable, systematically improvable methods to capture precise properties of systems interacting with a large number of other systems.
1 Introduction

Starting a few decades ago, and continuing apace today, enormous progress is being made in performing useful chemical simulations by decomposing large quantum mechanical calculations into recoupled subsystems. The state of the art generally consists of some kind of embedding of a fragment into the electrostatic environment of its neighbors (with various approaches to the exchange interaction),\textsuperscript{1–9} or a fragment-based decomposition of a reference wavefunction as a starting point for handling electron correlation,\textsuperscript{10–12} and all perhaps in combination with schemes for configurational sampling or techniques for handling redundancy in periodic systems.\textsuperscript{13–15} The literature chronicling the evolution of fragment-based methods is vast, and has been reviewed several times.\textsuperscript{16–19}

Notwithstanding all of this progress, a more favorable ratio of accuracy to computational cost is always desirable, in order to broaden the coverage of reliable simulations, especially if the phenomenon under investigation hinges on small energy differences. There exists a present need for an \textit{ab initio} scheme of recoupling quantum mechanical molecular systems that has a well-defined progression towards exactness, and which is flexible under approximation (perhaps subsuming some known fragment methods). Systematic improvability is the only way to rigorously demonstrate the reliability of a model in the context of a \textit{specific} problem.

One shortcoming of presently available fragment-based electronic structure methods with regard to cost is that electron correlation (if included) is computed at the level of individual electrons. Reliance on integrals describing interactions between individual electrons will render any high-order correlation scheme inefficient because the structure of the local relaxations that accompany single-electron fluctuations are effectively recomputed for each separate interaction between them.

Given the relative complexity of intra-fragment electronic correlation, as compared to the simple picture of the coupled dipolar (\textit{etc.}) fluctuations for inter-fragment interactions, it is reasonable to view the electronic coordinates of component fragments in terms of collective motions. This article describes the formal infrastructure necessary to generalize the coupled-cluster (CC) algorithm to operate on a space of collective coordinates of general fragments. By making truncations in the context of electronically correlated basis states for the fragments, high-energy local arrangements are expunged from consideration, and an effective suppression of individual degrees of freedom results. The proposed scheme is illustrated pictorially in Fig. 1,
Figure 1: A pair of interacting molecules can be viewed in terms of individual electrons fluctuating between local orbitals, whereby a “primary” excitation (denoted with an asterix) is accompanied by a number of other connected nominal excitations that actually account for relaxations of other electrons. The same interaction can also be conceived of in terms of fluctuations of the fragments between electronically correlated states, which inherently contain these relaxations. Given the large energetic scale of intra-fragment correlation, relative to the interaction between fragments, the relaxations that accompany local fluctuations that build inter-fragment interactions should be largely similar across interactions and need only be computed once for each fragment.

whereby the degrees of freedom at the global scope of a computation are internally correlated excitations of entire subunits. Local relaxations that accompany the primary motion of a fluctuating electron are computed once for each fragment, and the effects are permanently folded into the effective Hamiltonian. The strong intra-fragment correlations become constant features of the low-energy part of the fragment state spaces, reducing the dimensionality of the problem. By defining fragment fluctuation operators (analogues of paired field operators), the CC formalism may be applied, which is a quite general wavefunction (see, for example, vibrational CC$^{20–22}$).

The basis of internally correlated fragment states will be referred to as the excitonic basis, since this is the conceptual site basis from which Dirac-Frenkel excitons are built. The general concept of working with fragment states is not new; it is the basis of molecular perturbation theory, and it figures prominently in the formal development of symmetry-adapted perturbation theory and the more recently developed molecular cluster perturbation theory. However, the implementations of these methods still proceed in terms of a Hamiltonian described in the one-electron basis. In low-order perturbation theory, there is indeed no computational savings in transforming the Hamiltonian because the implicit transformation may be incorporated into the non-iterative Hamiltonian action at no additional cost.
The motivations for proceeding beyond low-order perturbation theory, however, are manifold. To begin with, long-range induction and other cooperative effects can be substantial and occur at relatively high orders (e.g., 4th) of perturbation theory.\textsuperscript{24,25} In addition to this, one expects further errors if polarizabilities from mean-field descriptions of the fragments are used, since these are known to be quite sensitive to correlation level,\textsuperscript{26} given that excitations energies control the “stiffness” of a charge distribution (denominators in perturbation theory). There is also some dynamical screening/cooperation between charge fluctuations, collectively known as many-body dispersion (a “body” is a fragment), which are missing at low orders of perturbation theory, and this has recently been shown to be important.\textsuperscript{27}

It is important to also mention the success of the general paradigm of coupling reduced state spaces of correlated subsystem states as embodied in the density matrix renormalization group method and the more general class of tensor-network states.\textsuperscript{28–30} While we might anticipate lesser success when near neighbors are highly entangled with each other, a more efficient treatment of system-wide dynamical correlation should result from the exponential Ansatz, which cleanly separates connected (correlated) and disconnected (coincidental) simultaneous fluctuations.

To elucidate the potential of the proposed paradigm mechanistically, consider that dispersion forces conventionally require at least a connected double substitution, already exhausting the excitation level that is available in conventional CC with single and double substitutions (CCSD). Corrections to fragment polarizabilities due to local relaxations will show up first when higher substitutions are included, such as perturbative inclusion of connected triples [CCSD(T)], the so-called “gold-standard” of quantum chemistry. In contrast, if up to connected double substitutions of primitive electrons were to enter the \textit{fragment} wavefunctions, a global \textit{excitonic} CC wavefunction with up to double excitations (excitonic CCSD) would automatically include some contributions from connected quadruple primitive substitutions. For these reasons it is not unreasonable to suggest that a practicable method might be built that can exceed the accuracy of a hypothetical conventional CCSD(T) calculation on systems that are well out of reach for even standard CCSD.

Another perspective on the justification for treating intra- and inter-fragment correlation on different footings is that the effective multipolar interactions between fragment fluctuations are orders of magnitude weaker than the bare Coulomb potential that is relevant to correlations.
within a fragment. The fluctuations of individual electrons within a couple of Ångstrom of one another are highly entangled, whereas fluctuations separated by great distances are described well as being a small perturbation away from independent.

As is familiar from local-correlation methods operating on primitive electronic coordinates, it will also be possible to implement index restrictions that further simplify interactions on the basis of the distance between the fragments involved. Similarly, the established linear response and equation-of-motion formalisms remain available to handle global excited states in terms of fragment excitations on top of the globally correlated ground state. The ability to straightforwardly proceed from ground-state to excited-state calculations is an important distinction with respect to incremental methods.

In this article, we provide the essential equations for an abstracted variant of CC theory that operates in a basis of fragment fluctuations. This establishes a notation that will be a common language with a companion paper that focuses specifically on the exact transformation of the Hamiltonian for electronic systems into the necessary form. In order to succinctly demonstrate that the proposed paradigm is promising, comparative timings are given here for systems composed of “molecules” that are internally constructed of coupled harmonic oscillators.

2 Theory

2.1 General Notation

Sets will be abbreviated as \( \{a_i\} \), for example, to represent all \( a_i \) corresponding to those values of \( i \) that are defined for a mapping \( a \). Lower-case latin letters are used for integer indices, and upper-case latin letters are used for indices that are ordered tuples of integers, for example, \( I = (i_1, \cdots, i_{\ell I}) \), where \( \ell I \) is the length of tuple \( I \), and \( i_1 < i_2 < \cdots < i_{\ell I} \). Any summation implicitly runs over all values of an index that are allowed by the mapping to which the index is attached in the summand.

In order to simplify the means by which states on different enumerated fragments are referenced, we will collect basis states of all fragments into a single set \( \{|\psi_i\rangle\} \), with a running integer index that first enumerates the states states of fragment 1, and then fragment 2, and so forth. If we wish to indicate that a state belongs to a specific fragment \( m \), then the notation \( |\psi_{im}\rangle \) is interpreted as placing a restriction on the value of \( i \). When used as a free index, such
as in denoting a set \( \{ |\psi_{i_{m}}\rangle \} \), or in the summation \( \sum_{i_{m}} \), it runs over all values consistent with this restriction. \( \{ |\psi_{i_{m}}\rangle \} \) is therefore the set of all basis states of fragment \( m \), which is a strict subset of \( \{ |\psi_{i}\rangle \} \).

### 2.2 Fluctuation Operators

Consider a generic super-system composed of \( N \) fragments. Given a complete basis \( \{ |\psi_{i_{m}}\rangle \} \) for the many-body state space of each fragment \( m \), we start with the assumption that the super-system state space is completely spanned by a set of states \( \{ |\Psi_{I}\rangle \} \), each having the form

\[
|\Psi_{I}\rangle = |\psi_{i_{1}} \cdots \psi_{i_{N}}\rangle
\]  

with \( I = (i_{1}, \cdots i_{N}) \). This notation is intended to imply, foremostly, that \( |\Psi_{I}\rangle \) is tensor-product-like in structure, such that it is meaningful say that fragment \( m \) is in state \( |\psi_{i_{m}}\rangle \). By collecting the fragment state labels into a single ket, it is implied that this is a valid state for the overall system, having proper inter-particle exchange symmetry among the primitive coordinates (e.g., electrons). The fact that the indexing of the sub-indices \( i_{m} \) of tuple \( I \) coincides with our notation for restricting an index to a specific fragment is a convenient coincidence that does not lead to ambiguity, since the first member of \( I \) does, in fact, refer to fragment 1, etc.

We next assert the existence of a set of fluctuation operators \( \{ \hat{\tau}_{i_{m}}^{j_{m}} \} \), where the upper and lower indices of each operator identify two states \( |\psi_{i}\rangle \) and \( |\psi_{j}\rangle \), which must belong to the same fragment (possibly the same state). The action of \( \hat{\tau}_{j_{m}}^{i_{m}} \) onto basis state \( |\Psi_{K}\rangle \) is defined as changing the state of the \( m \)-th fragment according to

\[
\hat{\tau}_{j_{m}}^{i_{m}} |\psi_{k_{1}} \cdots \psi_{k_{m}} \cdots \psi_{k_{N}}\rangle = \delta_{j_{m},k_{m}} |\psi_{k_{1}} \cdots \psi_{i_{m}} \cdots \psi_{k_{N}}\rangle
\]  

This action is constructed to be reminiscent of a number-conserving pair of field operators onto a single-determinant electronic state, such that the null state results if the lower (“destruction”) index corresponds to an “empty” fragment state. These operators have the following commutation relation by construction

\[
[\hat{\tau}_{j}^{i}, \hat{\tau}_{l}^{k}] = \delta_{jk} \hat{\tau}_{i}^{i} - \delta_{il} \hat{\tau}_{j}^{k}
\]
This is shown from the definition in eq. (2) by noting, first, that operators on different fragments commute, and, second, that a string of two operators on the same fragment gives null if the lower index of the left operator does not match the upper index of the right operator.

The assumptions that a set of tensor products of such states builds a complete basis for the super-system space, and that the asserted fluctuation operators are well defined in that space, are points that need to be proven for different classes of systems. The effort to show this and arrive at exact working expressions (also amenable to approximations) for fragment-decomposed electronic systems is found in the companion article. For the model fragments explored in this work (closed systems of distinguishable degrees of freedom), these assumptions are trivially valid.

2.3 Coupled-cluster Ansatz

According to the foregoing definition of the fluctuation operators, any basis state $|\Psi_I\rangle$ may be reached from any other basis state $|\Psi_J\rangle$ via a string of $N$ (or fewer) fluctuation operators. Combined with the assumption of completeness of this basis, it is then straightforward to show that an arbitrary super-system state has a unique resolution in terms of the full $N$-th order CC Ansatz (Full CC, FCC) applied to a reference state $|\Psi_O\rangle$ conforming to $\langle \Psi_{FCC}|\Psi_O\rangle \neq 0$, as

$$|\Psi_{FCC}\rangle = e^\hat{T} |\Psi_O\rangle$$

(4)

We have hereby identified the tuple $O = (o_1, \cdots, o_N)$ as special, in that $|\psi_{o_m}\rangle$ is taken to be the reference state of fragment $m$. The operator $\hat{T}$ consists only of fluctuations away from the reference, denoted $\hat{\tau}_{o_m}^{i_m}$ with $i_m \neq o_m$, referred to specifically as excitations

$$\hat{T} = \sum_m \sum_{i_m \neq o_m} t_{i_m} \hat{\tau}_{o_m}^{i_m} + \sum_{m_1 < m_2} \sum_{i_{m_1} \neq o_{m_1}} \sum_{i_{m_2} \neq o_{m_2}} t_{i_{m_1} i_{m_2}} \hat{\tau}_{o_{m_1}}^{i_{m_1}} \hat{\tau}_{o_{m_2}}^{i_{m_2}} + \cdots$$

(5)

The notation $m_1 < m_2$ indicates that the summation runs over all unique pairs (etc.) of fragments. As with traditional CC theory, excitation operators all clearly commute with one another.

As an approximation, the expansion of $\hat{T}$ will generally be truncated at finite fragment order, with the terms written explicitly in eq. (5) being those retained in the generalized excitonic
CCSD variant. In this case, single substitutions are associated with monomers, and doubles are associated with dimers, etc. An interesting analogue to Hartree–Fock theory that would capture long-range induction, using polarizabilities from correlated levels of theory, would be the use of only single excitations in $\hat{T}$ (CCS). Models beyond CCS introduce entangled fluctuations among internally correlated fragment states, accounting for dispersion forces, etc., in a manner that is both self-consistent and size-consistent. In all cases, since the states $\{|\psi_i\rangle\}$ are internally correlated, the most powerful local correlations are solved for with the introduction of the super-system basis, and the reference already includes a large fraction of correlation. The state spaces of the fragments are intended to be truncated according to schemes that consider the balance of cost against accuracy of the desired property (perhaps local to a region of interest).

### 2.4 Hamiltonian

With a general wavefunction Ansatz available, the central task is to iteratively determine the amplitudes $t_{im}$, $t_{im_1im_2}$, $\cdots$ that approximate an eigenstate of Hamiltonian $\hat{H}$. More precisely, the residual of the eigenstate condition must lie outside the space of variations. This involves the familiar step of evaluating the action of the similarity-transformed Hamiltonian $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ onto the reference $|\Psi_O\rangle$ in the context of a well-chosen non-linear optimization algorithm. The amplitude update is related to the projection of the result of this action into the space spanned by excitations up to the specified Ansatz order. Technically, convergence is met when this projection is suitably small, though this is usually signaled by the energy becoming approximately stationary between iterations.

This brings us now to the subject of the Hamiltonian itself. In order to avoid expensive recourse to the primitive degrees of freedom during the amplitude iterations, $\hat{H}$ must also be written as an expansion in terms of strings of the fluctuation operators

$$\hat{H} = \sum_m \sum_{i_m,j_m} H_{i_m,j_m} \hat{T}^{i_m}_{j_m} + \sum_{m_1<m_2} \sum_{i_{m_1},j_{m_1},i_{m_2},j_{m_2}} H_{i_{m_1}i_{m_2},j_{m_1}j_{m_2}} \hat{T}^{i_{m_1}}_{j_{m_1}} \hat{T}^{i_{m_2}}_{j_{m_2}} + \cdots \quad (6)$$

The elements $H_{i_m,j_m}$ build the Hamiltonian matrix for fragment $m$, and the higher-order terms are responsible for couplings between fragments (up to $N$-th order, in principle, depending on the kind of system). If the Hamiltonian is written as such, then the generalized normal ordering of the nested commutators of the Baker-Campbell-Hausdorff (BCH) expansion of $e^{-\hat{T}}\hat{H}e^{\hat{T}}$ can
be neatly divided into the usual four parts: (1) terms that result in the null state when acted
onto $|\Psi_O\rangle$, (2) a constant, (3) terms representing excitations within the specified Ansatz, and
(4) terms representing excitations outside (e.g., higher) than the Ansatz. Part (2) is the pseudo-
energy at any iteration, part (3) determines the update to the amplitudes, and parts (1) and
(4) need not be computed. As with traditional CC methods, deriving optimal formulas and
algorithms for these evaluations demands substantial work, which will be undertaken in the
future.

We have now added a third assertion, that the system Hamiltonian can be written in terms
of fragment fluctuations, to our original two, which concerned basis completeness and existence
of the fluctuation operators. It is likely possible to prove that such a form of $\hat{H}$ always exists for
broad classes of systems, relying on only benevolent assumptions; however, while interesting, it
would be useless without an explicit form and a computational recipe for the scalar coefficients
therein. Therefore, we leave this as an assertion to be shown on a case-by-case for each class
of systems (e.g., all fragment-decomposed electronic systems). For the model systems in this
article, this will be trivial, but, for electronic systems that may overlap and transfer charge
(possibly also having linear dependencies in the one-electron basis), the exercise is more intense
and is undertaken in the companion article.

Finally, it is important that the BCH expansion naturally truncates at some low order, so
that evaluation of the amplitude updates has manageable computational cost. As in conven-
tional CC theory, if the Hamiltonian itself contains only few-body terms, the requirement for
this self-truncation will be fulfilled if the commutator of any two fluctuations is an operator
that has both the same excitation rank as the sum of the original two and a fragment rank
of less than two.\textsuperscript{38} That the fragment rank is reduced by commutation is already manifest in
eq. (3). Excitation rank of a string of fluctuations can be defined by subtracting the number
of upper indices that refer to a fragment reference state from the number of lower such indices
(roughly, number of excitations minus number of de-excitations). In those commutators that
are not already zero, these numbers are either individually preserved or each is decremented by
one, thus preserving excitation rank. Therefore, the BCH expansion must naturally truncate
for this generalized CC model.
3 Results from Model Molecules

In order to illustrate the intended promise of computational efficiency, let us explore a simple model of an *a priori* pairwise fragment Hamiltonian. At a philosophical level, by making a clean break from the target electronic systems, this highlights the level of abstraction at which CC theory is being generalized. On a practical level, this gives us the freedom to choose a Hamiltonian for which the exact eigensolutions can be obtained, for purposes of comparison.

Before discussing the fragments themselves, we write a generic Hamiltonian for $N$ closed systems (with distinguishable internal coordinates) distributed in one dimension, coupled only by the longitudinal dipole–dipole interaction

$$
\hat{H} = \sum_{m} \hat{H}^{(m)} + \sum_{m_1 < m_2} k^{(m_1,m_2)} \hat{\mu}^{(m_1)} \hat{\mu}^{(m_2)}
$$

$\hat{H}^{(m)}$ is the Hamiltonian of the $m$-th fragment in isolation, $\hat{\mu}^{(m)}$ is its dipole operator along the super-system axis, and $k^{(m_1,m_2)} = \frac{-2E_h a_0}{\epsilon^2 R_{m_1 m_2}}$ depends on the distance $R_{m_1 m_2}$ between fragments $m_1$ and $m_2$ ($E_h$, $a_0$, and $\epsilon$ are atomic units of energy, length and charge, respectively).

We now posit for each fragment $m$ a set of orthonormal states $\{|\psi_{i_m}\rangle\}$ of its fixed number of internal degrees of freedom. The tensor product of these sets is the set of orthonormal states $\{|\Psi_I\rangle\}$, whose span defines the super-system space for this model. By considering separately the cases where, one, two, etc., fragment states differ between the bra and ket of a matrix element, it is straightforward to show that the Hamiltonian projected into this super-system basis may be rewritten exactly as

$$
\hat{H} = \sum_{m} \sum_{i_m,j_m} H_{i_m,j_m} \hat{z}_{i_m} \hat{z}_{j_m} + \sum_{m_1 < m_2} \sum_{i_{m_1},j_{m_1},i_{m_2},j_{m_2}} k^{(m_1,m_2)} \mu_{i_{m_1},j_{m_1}} \mu_{i_{m_2},j_{m_2}} \hat{z}_{i_{m_1}} \hat{z}_{i_{m_2}}
$$

$$
H_{i_m,j_m} = \langle \psi_{i_m} | \hat{H}^{(m)} | \psi_{j_m} \rangle \quad \mu_{i_m,j_m} = \langle \psi_{i_m} | \hat{\mu}^{(m)} | \psi_{j_m} \rangle
$$

This is in the form that we have demanded for the excitonic CC scheme, and it intuitively has maximum fragment rank of two.

We now turn our attention to the Hamiltonians and dipole operators of the individual fragments. It will be convenient to let each fragment be described as a system of linearly coupled harmonic oscillators, where we freely choose the internal coupling parameters as proxies
for general interactions of internal coordinates. If we further consider the coordinate of each
primitive oscillator as representing the distance between two opposing charges in the direction
of the inter-fragment axis, then the dipole operators of the fragments are consequently defined
(details to come). This model is convenient because the inter-fragment dipole–dipole coupling
may also be decomposed in terms of linear couplings between all pairs of oscillators on distinct
fragments. A further advantage is that all necessary integrals are easily evaluated.

Since the overall system consists entirely of linearly coupled harmonic oscillators, diagonal-
ization of the matrix of coupling constants (for a given set of inter-fragment distances) can be
used to obtain the ground-state energy to within machine precision with little computational
effort. The utility of having this exact solution available is in being able to assess errors pre-
cisely. It should be made clear, however, that this method of exact solution relies on a structure
to the problem that is lost upon projection into a basis. The dimension of the basis-projected
super-system Hamiltonian scales exponentially with \(N\), and it should be anticipated that, once
projected, systems of many such model molecules present similar algorithmic complexity as
systems of real molecules, per degree of freedom. Along these lines, it is worthwhile to point
out that the sparsity of linear couplings between oscillators due to the dipolar selection rules is,
in fact lost upon transformation to an internally correlated basis. There is no obvious special
structure to the Hamiltonian that indicates that the performance gain here is a special case,
and so we expect this paradigm to be transferable to molecules. In the weak coupling limit
(charge-transfer suppressed), the Hamiltonians of interacting molecules may be written in this
same form, only with different values of the generally multipolar integrals.

The computational efficiency of the excitonic CC scheme will be demonstrated by comparing
it to a CC calculation that operates on fluctuations of the primitive oscillators that build
the fragments. This “control” part of the experiment is intended to mimic the conventional
practice of working with creation and annihilation operators for individual electrons. In these
calculations the reference state has each primitive oscillator in its isolated ground state. For
the “test” part of the experiment, we must chose bases for the many-body state spaces of
the fragments. The internally correlated basis \(\{|\psi_{im}\}\) for fragment \(m\) is taken here to be the
set of exact energy eigenstates of the isolated fragment. These states and the exact values
of the matrix elements of \(\hat{H}^{(m)}\) and \(\hat{\mu}^{(m)}\) in this basis are available via the aforementioned
diagonalization of the internal coupling matrices for the individual fragments.
For these model systems, both the primitive and excitonic variants have abstractly the same form (each primitive oscillator can be mapped to a fragment), such that exactly the same computer program is used for the control and test, only with input tensors of dramatically different dimensions. A completely in-house Python-based implementation of the CC algorithm is used; evaluation of the BCH expansion is coded in C and called as a shared library from a generic quasi-Newton/DIIS driver.\textsuperscript{38} For the BCH evaluation, expressions for the necessary matrix elements of nested commutators with respect to the reference and excitation manifold were arrived at by straightforward algebraic application of eq. (3), the derivation and implementation of which were both done by hand. Though a generalized diagrammatic approach would certainly be more elegant and expose the optimal factorizations, our purpose is only to provide relative timings here. Optimization was indeed sacrificed at some points to produce code that is most easily read and least prone to error, within the restriction of not introducing loops of spuriously high scaling. It is worth noting that the fragment-local nature of the fluctuations provides what would map on to an index restriction in conventional diagrams, massively simplifying the algebraic approach, and also producing loops that scale maximally with the third order of the system size, for a fixed number of states per fragment. The timings were run on a single 2.20 GHz Intel Xeon (E5) core, and all quantities were kept in core memory.

Our test systems consist of linear chains of 2 to 30 oscillator-model molecules, equally spaced by either 5 or 10 $a_0$. Each such fragment consists of 8 internal oscillators with force constants spread evenly over the range of 1 to $2 E_h/a_0^2$ (increment of $1/7 E_h/a_0^2$). Each harmonic potential contains a particle with the same mass as an electron, and its coordinate is interpreted as the displacement of a charge of $-e$ relative one of $+e$. The coupling constant between each pair of internal oscillators has a positive (repulsive) value whose magnitude is $1/3$ of the difference between their force constants, such that oscillators with quite different force constants are also substantially mixed in the fragment reference states.

For any given system, the total energy and the energies of both possible reference states (primitive or excitonic) are well defined, aside from any approximations. The energy drop to the exact solution, relative to the corresponding reference, is much larger for the primitive case, where it is the entire correlation energy, as compared to the excitonic case, where only the inter-fragment interaction energy remains to be computed. For the systems described, the asymptotic energy correction (with respect to $N$) for the excitonic case is $-5.5 \times 10^{-4} E_h/\text{fragment}$ or
-8.5 \times 10^{-6} \text{E}_h/\text{fragment}, for 5 \ a_0 or 10 \ a_0 separation, respectively, whereas the respective corrections for the primitive case are -5.0 \times 10^{-2}\text{E}_h/\text{fragment} or -4.9 \times 10^{-2}\text{E}_h/\text{fragment}. Naturally, the excitonic CC correction depends much more strongly on the interaction strength and asymptotes to zero with separation.

In both cases, we allow single and double substitutions. Owing to the limited excitation level in the Ansatz, both the primitive and excitonic variants approach a finite inherent model error, even as the size of the basis set is increased to completeness (either number of states per oscillator or number of states per fragment, respectively). All reported timings are for the smallest basis (fastest timing) that is effectively reaches this basis set limit. This is evaluated by comparison to the exact solution. In principle, we assert convergence with respect to basis for a given system when the order of magnitude of the error is constant and the mantissa no longer changes in the second significant digit. For convenience, in practice, a threshold is established that is used for all system sizes for a given primitive or excitonic variant that overestimates the asymptotic value of this error (with respect to \(N\)) by a few percent, since the method error as a fraction of the CCSD energy correction is fairly independent of system size for larger \(N\). For the primitive variant, this threshold error fraction is roughly 1.7 \times 10^{-2} (for both spacings), and it is 2.6 \times 10^{-3} (5 \ a_0) or 4.2 \times 10^{-5} (10 \ a_0) for the excitonic variant. Irrespective of spacing or number of fragments, application of this criterion uniformly demands 9 states per fragment for the excitonic calculations and 4 states per oscillator for the primitive calculations (32 states per fragment). Any individual calculation is considered converged when the energy correction changes by less than 1 part in 10^8 between BCH updates of \(\hat{T}\). Note that the demanding convergence criteria used will further increase absolute timings beyond what may be necessary in realistic situations.

The computations times for each variant and inter-fragment spacing are plotted against the number of fragments in Fig. 2. The excitonic CCSD variant is seen to be a factor of 20 to 30 times faster than for the primitive variant for the larger numbers shown. The best fit monomials to the timings for the largest 15 systems are 0.0025 \ s \times N^{2.94} vs. 0.051 \ s \times N^{2.97} for 5 \ a_0 spacing and 0.0021 \ s \times N^{2.93} vs. 0.052 \ s \times N^{2.96} for 10 \ a_0 spacing, consistent with our expectation of 3rd-order scaling. This is in addition to the fact that the results from the excitonic CC calculations are 3 to 6 orders of magnitude more accurate on an absolute scale, depending on the spacing. Since the tighter basis-set convergence criterion for the excitonic
results are relative to an already smaller energy correction, the accuracy of the excitonic CC results is much better than that which could be demanded from the primitive CC results. The actual absolute error for the basis-converged excitonic calculation of the 30-fragment system was \(1.4 \times 10^{-6} \text{E}_h/\text{fragment}\) (5 \(a_0\)) or \(3.2 \times 10^{-10} \text{E}_h/\text{fragment}\) (10 \(a_0\)), as opposed to \(8.3 \times 10^{-4} \text{E}_h/\text{fragment}\) (5 \(a_0\)) or \(8.2 \times 10^{-4} \text{E}_h/\text{fragment}\) (10 \(a_0\)) for the primitive calculation.

Clearly ignored in this discussion is the price of computing the fragment-based Hamiltonian. While this could be a formidable task for a real system, it is important to recognize that it will nevertheless present a lower scaling than the global calculation. This topic is the subject of a companion article.

4 Conclusion

In this article we have laid out the theory and prospective advantages of basing a CC wavefunction on the fluctuations of fragments between internally correlated states. A numerical demonstration of the promise of this approach has been provided.

An important aspect of the excitonic CC model going forward is that it is theoretically independent of the level of electronic structure theory used to compute the excited states of

Figure 2: For two different spacings between linearly arranged “molecules,” the computational time for the CC algorithm operating on primitive subsystem coordinates is compared to the that for excitonic CC, which operates in terms of fluctuations between correlated subsystem eigenstates. Not only is the error associated with the excitonic model much smaller, but the computational time is much shorter. The connecting curves are best-fit monomials with non-integer exponents; all are described well as cubic functions.
the constituent fragments. Since it is not tied to any specific level of theory, it is not inherently
subject to the shortcomings of any given base method. In common with other frameworks,
such as ONIOM,\(^{39}\) a site of interest may be handled in more detail than other parts of the
system. For example, some small molecules undergoing reactions may be treated using multi-
reference methods, whereas less expensive methods suffice for the excited states of molecules
in the periphery, and all of this remains systematically improvable. Naturally, the flexibility to
have then entire quantum mechanical system subject to an external potential (e.g., molecular
mechanics embedding) is still available. A completely novel capability that may open up if the
method proves to be efficient enough is that the states of the fragment molecules might include
vibrational excitations.

The final formal challenge in applying the abstract machinery proposed here to realistic
systems is the mapping of the \textit{ab initio} Hamiltonian onto one written in terms of fragment
fluctuations, inclusive of exact handling of exchange and even potential linear dependencies
arising in the one-body basis. This is the subject of a companion paper that presents a general
solution to the problem in detail. By way of foreshadow, the number of terms in the exactly
transformed electronic Hamiltonian scales formally quartically, entering through a requirement
to perform computations on all possible tetramers. There will admittedly be cases where
this cost is prohibitive, but also a number of important cases where it is not. Quadratically
scaling approximate Hamiltonians (giving cubically scaling methods, as we have here) can be
constructed that still allow for inter-fragment charge resonance, possibly even creating covalent
linkages. Furthermore, it is also trivial to generally reduce the scaling also to quadratic to within
an arbitrarily small error tolerance. Finally, the vast majority of interactions occur between
systems that are not overlapping, and, for these purely Coulombic interactions, reusable single-
fragment information suffices to compute all such interactions.

In conclusion, the methods proposed here are almost assured to more efficiently provide
an accuracy that is comparable to or better than a conventional CC calculation of the same
substitution level. There are also many features of this work which hold promise as a framework
to build for finely tunable approximation schemes to capture precise properties of systems
interacting ever more realistically with a large number of other systems.
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