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Recursive scheme for order-by-order many-body perturbation theory

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The coupled-cluster method is used to recursively organize the calculations for nondegenerate order-by-order many-body perturbation theory. Application to correlation energy with Hartree-Fock zeroth-order state is presented. Commutator algebra is efficiently handled with the contraction theorem. When compared to standard diagrammatic methods, considerable simplifications are found beyond third order.

I. INTRODUCTION

With the establishment of the linked-cluster theorem of many-body perturbation theory, it has become customary to express perturbation corrections at various orders with the help of linked diagrams. Involving a number of rules one proceeds from such diagrams to algebraic expressions. For example, energy expressions are connected in the sense that their sums cannot be written as products of sums with decoupled summation indices. This organization of correction terms guarantees the explicit avoidance of terms that can scale improperly with the size of the system considered.

However, there are at least two disadvantages to this approach. First, the number of diagrams, even with antisymmetrized interaction lines, increases horrendously with increasing order of perturbation. For example, in the third order only three diagrams appear, whereas in the fourth order, there are already thirty-nine distinct diagrams even when a Hartree-Fock zeroth-order state is used.[1] Apart from sheer labor of enumeration or clever design of a computer program, this seems unsatisfactory from an operational standpoint. Second, if one wishes to compute a high-order perturbative correction at all, it will be typically preceded by calculations of all lower orders since one is interested in its relative magnitude. However, the linked-cluster theorem prescribes, in essence, the writing of all diagrams in each order without exploiting any work done at the lower orders. Therefore, it would be highly desirable, on the one hand, to arrange for a lesser proliferation of terms at higher orders, and, on the other hand, to organize the work in such a manner that quantities calculated as building blocks at lower orders can be used again at higher orders.

We wish to present a formulation of order-by-order perturbation theory that goes a long way towards achieving the two desiderata raised above. The starting point is the coupled-cluster method. Its intimate connection with many-body perturbation theory can be exploited to calculate the cluster operators and energies order-by-order, with expressions that involve cluster operators already obtained at lower orders. Using a Hartree-Fock zeroth-order state, we give explicit expressions for correlation energy corrections through fourth order. A comparison with conventional many-body perturbation theory is made. Central to the derivation is the implementation of the contraction theorem for the reduction of commutators of operator strings. This powerful algebraic tool was presented and proven in the preceding paper[2] (hereafter referred to by I). Finally, relations to other approaches are discussed.

II. DEFINITIONS AND NOTATIONS

The perturbed many-body Hamiltonian is

$$H=H_0+H' \;. \tag{1}$$

H_0 is the zeroth-order Hamiltonian given by

$$H_0=\sum_\mu \epsilon_\mu a^\mu a_\mu \;, \tag{2}$$

where the sum is over both occupied and unoccupied states. We adopt the convention that such summations have indices μ, ν, λ, or σ. Occupied states are indicated by $\alpha,\beta,\gamma,\delta,\ldots,$ and unoccupied states by $r,s,p,q,\ldots.$ In Eq. (2) a^μ stands for the Hermitian conjugate of the Fermion annihilation operator $a_\mu^\dagger$, and ϵ_μ is the orbital energy associated with the μth state. The reference state Φ (with respect to which the designations "occupied" and "unoccupied" are made) is an eigenfunction of H_0:

$$H_0\Phi=E_0\Phi \;. \tag{3}$$

In creation and annihilation language we can write

$$\Phi = \prod_{\alpha} a^{\alpha} | 0 \rangle , \tag{4}$$

with $|0\rangle$ the vacuum state. The zeroth-order energy E_0 is given by

$$E_0 = \langle \Phi | H_0 | \Phi \rangle = \sum_{\alpha} \epsilon_{\alpha} . \tag{5}$$

Turning next to the perturbation part of the Hamiltonian, H' can be expressed as

$$H' = U + V . \tag{6}$$

If H_0 is assumed to be the Hartree-Fock Hamiltonian, and if H' exclusively describes correlation effects, then U is the one-particle operator

$$U = - \sum_{\lambda\sigma\gamma} v^{\lambda\gamma}_{\sigma\gamma} a^{\lambda} a_{\sigma} , \tag{7}$$

where the matrix elements are given by

$$v^{\mu\nu}_{\lambda\sigma} = \langle \mu\nu | r^{-1}_{12} | \lambda\sigma \rangle - \langle \mu\nu | r^{-1}_{12} | \sigma\lambda \rangle . \tag{8}$$

V is the two-electron operator,

$$V = \tfrac{1}{4} \sum_{\mu\nu,\lambda\sigma} v^{\mu\nu}_{\lambda\sigma} a^{\mu} a^{\nu} a_{\sigma} a_{\lambda} . \tag{9}$$

We observe that the matrix elements of Eq. (8) are antisymmetric under index interchanges:

$$v^{\mu\nu}_{\lambda\sigma} = - v^{\nu\mu}_{\lambda\sigma} = - v^{\mu\nu}_{\sigma\lambda} . \tag{10}$$

III. THE COUPLED-CLUSTER METHOD

In the coupled-cluster method, the many-body wave function is expressed as

$$\Psi = e^{T} \Phi , \tag{11}$$

where the cluster operator is given as

$$T = \sum_{m} T_m . \tag{12}$$

The components T_m are defined as

$$T_1 = \sum_{r\alpha} t^{r}_{\alpha} a^{r} a_{\alpha} , \tag{13}$$

$$T_2 = \tfrac{1}{4} \sum_{rs,\alpha\beta} t^{rs}_{\alpha\beta} a^{r} a^{s} a_{\beta} a_{\alpha} , \tag{14}$$

etc. The wave function Ψ is sought to satisfy the Schrödinger equation

$$H\Psi = E\Psi . \tag{15}$$

With Ψ of the form of Eq. (11) and a multiplication of Eq. (15) from the left with $\exp(-T)$ we obtain the equivalent form

$$(e^{-T} H e^{T}) \Phi = E \Phi . \tag{16}$$

The operator in parentheses, which has the form of an effective operator, is non-Hermitian because $\exp(T)$ is not unitary. Equations for E and T are obtained by projecting Eq. (16) against Φ and particle-hole (ph) excitations thereform, defined by

$$\Phi^{r}_{\alpha} = a^{r} a_{\alpha} \Phi , \tag{17}$$

$$\Phi^{rs}_{\alpha\beta} = a^{r} a^{s} a_{\beta} a_{\alpha} \Phi , \tag{18}$$

etc. In practice a truncated set of T_m is retained in Eq. (12) and only projections associated with the nonzero components are included. Thus equations of the following form are found:

$$E = \langle \Phi | H e^{T} | \Phi \rangle , \tag{19}$$

$$\langle \Phi^{r}_{\alpha} | e^{-T} H e^{T} | \Phi \rangle = 0 , \tag{20}$$

$$\langle \Phi^{rs}_{\alpha\beta} | e^{-T} H e^{T} | \Phi \rangle = 0 , \tag{21}$$

etc. We dropped $\exp(-T)$ in Eq. (19), since this factor does not affect the result of projections against Φ. Considerable simplifications to the equations arise because of the special form adopted for T. The major, and most significant simplification is the reduction of the operator $\exp(-T)$ $H \exp(T)$ to a *finite* commutator series, regardless of the number of particles or truncations in Eq. (12). This feature makes the coupled-cluster method manifestly connected in the sense that E and the projections such as Eqs. (19) and (20) do not contain any sums expressible as a product of sums. Not surprisingly, this connectedness is the basis for a close relationship with the linked-cluster expansion in many-body perturbation theory. For details and appropriate references, we refer to I, in particular its Refs. 1–4.

IV. ORDER-BY-ORDER PERTURBATION THEORY

We can go one step further and use the coupled-cluster method to formulate finite-order perturbation calculations. To set the stage let us use Eq. (19) to express the perturbation energy ΔE in the form

$$\Delta E = E - E_0 = \langle \Phi | H' (1 + T_1 + T_2 + \tfrac{1}{2} T_1 T_1) | \Phi \rangle . \tag{22}$$

Because of the two-particle character of H' only T_1 and T_2 appear in the expression for ΔE. In order to now compute ΔE to successive orders in H',

$$\Delta E = \Delta E^{(1)} + \Delta E^{(2)} + \Delta E^{(3)} + \cdots , \tag{23}$$

we see from Eq. (22) that T needs to be computed to successive orders in H',

$$T = \overset{(1)}{T} + \overset{(2)}{T} + \overset{(3)}{T} + \cdots . \tag{24}$$

Equations for $T^{(n)}$ must be obtained by manipulating the Schrödinger equation. (In the text, order index to T will be a superscript.) Starting from Eq. (16), we write

$$(H+[H,T]+\tfrac{1}{2}[[H,T],T]+\cdots-E)\Phi=0\,. \tag{25}$$

As indicated in I, there is series termination after the quadruple commutator involving V only. With Eq. (1) and the result of I that multiple commutators involving H_0 vanish, we can also express Eq. (25) as

$$(E_0+[H_0,T]-E+H'+[H',T]+\cdots)\Phi=0\,. \tag{26}$$

But

$$[H_0,T]\Phi=(H_0-E_0)T\Phi\,, \tag{27}$$

and therefore Eq. (26) can be rearranged to give

$$(E_0-H_0)T\Phi=(E_0-E)\Phi+(H'+[H',T]+\cdots)\Phi\,. \tag{28}$$

To now obtain an explicit expression for T, we introduce the reduced resolvent of H_0 (Ref. 3):

$$R_0=P(E_0-H_0P)^{-1}\,, \tag{29}$$

where

$$P=1-|\Phi\rangle\langle\Phi| \tag{30}$$

is the projection operator onto the orthogonal complement of Φ. When both sides of Eq. (28) are multiplied by R_0, we get the result

$$T\Phi=R_0(H'+[H',T]+\tfrac{1}{2}[[H',T],T]+\cdots)\Phi\,. \tag{31}$$

At this point, the need for the assumption of a nondegenerate ground state arises. Otherwise R_0 could be singular. By projecting Eq. (31) against different ph excitations, we get equations for the cluster components:

$$t^{r}_{\alpha}=\langle\Phi^{r}_{\alpha}|T|\Phi\rangle\,, \tag{32}$$

$$t^{rs}_{\alpha\beta}=\langle\Phi^{rs}_{\alpha\beta}|T|\Phi\rangle\,, \tag{33}$$

etc.

Thus far, we have only reshuffled terms. However, the Schrödinger equation in this form affords a calculation of T to a given order of H'. Since $T^{(n)}$ is the $(H')^n$ term in T, with $T^{(0)}=0$, Eq. (31) immediately gives

$$\overset{(1)}{T}=R_0H'\Phi\,, \tag{34}$$

and for $n\geqslant 2$ we have

$$\overset{(n)}{T}\Phi=R_0\left([H',\overset{(n-1)}{T}]+\tfrac{1}{2}\sum_{j=1}^{n-2}[[H',\overset{(j)}{T}],\overset{(n-j-1)}{T}]+\cdots\right)\Phi\,. \tag{35}$$

Two observations about this equation are in order. First, $T^{(n)}\Phi$ is expressed as a multiple commutator series involving $T^{(1)}$ through $T^{(n-1)}$. We saw in I that such commutators are expressible as contractions, which lead to the connectedness of sums as discussed above. Therefore, if $T^{(1)}$ through $T^{(n-1)}$ are connected, then $T^{(n)}$ is connected. $T^{(1)}$ is obviously connected since R_0 is diagonal and thus does not affect the connectedness. Therefore all $T^{(n)}$ are connected.

Second, because of the connectedness of $T^{(n)}$ the energy ΔE is also expressible as an expansion of connected terms. Specifically, the contribution of $\Delta E^{(n)}$ to nth order in H' can be written as

$$\Delta E^{(n)}=\left\langle\Phi\middle|H'\left(\delta_{n1}+\overset{(n-1)}{T_1}+\overset{(n-1)}{T_2}+\frac{1}{2}\sum_{j=1}^{n-2}\overset{(j)}{T_1}\,\overset{(n-j-1)}{T_1}\right)\middle|\Phi\right\rangle. \tag{36}$$

This is a powerful result. Using Eq. (35) we can compute $T^{(n)}$ $(n\geqslant 2)$ from $T^{(1)}$ to $T^{(n-1)}$. With Eq. (36), we have a very compact expression of $\Delta E^{(n)}$ in terms of $T^{(1)}$ through $T^{(n-1)}$. Manifestly connected expressions appear at all orders, thanks to the commutators. We also achieve major reductions in computational effort, in particular at higher than third order, because of the appearance of multiple commutators in the expressions for $T^{(n)}$. As explained in Ref. 4 of I, this reduction is connected with the summation of individual diagrams within some order of perturbation theory via the so-called factorization theorem. This theorem states that diagrams with the same connection patterns (leading to the same numerators) but with different orderings of their interaction lines (leading to different energy denominators) can be summed to a product in which individual factors are evaluated as separate diagrams. This summability can occur at fourth order and up, and it becomes increasingly beneficial at higher orders. For an exposition of this and other points, including the formal equivalence to the linked-cluster theorem, we refer to Ref. 4 of I. It should be pointed out that the present recursive scheme given by Eqs. (34), (35), and (36) is implicit in Coester's 1958 paper,[4] but to our knowledge the details have never been published.

V. EXAMPLE: CORRELATION ENERGY THROUGH FOURTH ORDER

We will now illustrate above approach by calculating $\Delta E^{(1)}$ through $\Delta E^{(4)}$ with H' as defined by Eqs. (6)–(10), the so-called Møller-Plesset partitioning of the Hamiltonian.

From Eq. (36) we immediately have

$$\Delta E^{(1)}=\langle\Phi|H'|\Phi\rangle\,, \tag{37}$$

which reduces to

$$\Delta E^{(1)}=-\tfrac{1}{2}\sum_{\alpha\beta}v^{\alpha\beta}_{\alpha\beta}\,, \tag{38}$$

$(E_0+\Delta E^{(1)})$ is the Hartree-Fock energy.

Next, to obtain $\Delta E^{(2)}$, we need to invoke Eq. (34). The action of H' on Φ produces

$$H'\Phi=U\Phi+V\Phi=-\tfrac{1}{2}\sum_{\alpha\beta}v^{\alpha\beta}_{\alpha\beta}\Phi-\sum_{\gamma,r\alpha}v^{r\gamma}_{\alpha\gamma}\Phi^{r}_{\alpha}+\Bigg(\sum_{\gamma,r\alpha}v^{r\gamma}_{\alpha\gamma}\Phi^{r}_{\alpha}+\tfrac{1}{4}\sum_{rs,\alpha\beta}v^{rs}_{\alpha\beta}\Phi^{rs}_{\alpha\beta}\Bigg)\,, \tag{39}$$

showing the cancellation of the single ph excitation from $U\Phi$ and $V\Phi$. We thus find

$$\overset{(1)}{T}\Phi=R_0H'\Phi=\tfrac{1}{4}\sum_{rs,\alpha\beta}\frac{v^{rs}_{\alpha\beta}}{\epsilon_\alpha+\epsilon_\beta-\epsilon_r-\epsilon_s}\Phi^{rs}_{\alpha\beta}\,. \tag{40}$$

We will next introduce the notations

$$\epsilon^{rs\ldots}_{\alpha\beta\ldots}=\epsilon_\alpha+\epsilon_\beta+\cdots-\epsilon_r-\epsilon_s-\ldots \tag{41}$$

and $T^{(n)}_m$ for the m-particle cluster operator of order n in H', with coefficients $t^{(n)rs\ldots}_{\alpha\beta\ldots}$ defined by

$$\overset{(n)}{T}_m\Phi=\left(\frac{1}{m!}\right)^2\sum_{rs\ldots,\alpha\beta\ldots}\overset{(n)}{t}{}^{rs\ldots}_{\alpha\beta\ldots}\Phi^{rs\ldots}_{\alpha\beta\ldots}\,, \tag{42}$$

with the summation over all m-tuple ph excitations. It is convenient to choose, without loss of generality, all t coefficients to be antisymmetric under interchange of any pair of hole or particle indices:

$$\overset{(n)}{t}{}^{r\ldots s\ldots}_{\alpha\ldots\beta\ldots}=-\overset{(n)}{t}{}^{s\ldots r\ldots}_{\alpha\ldots\beta\ldots}=-\overset{(n)}{t}{}^{r\ldots s\ldots}_{\beta\ldots\alpha\ldots}\,. \tag{43}$$

Looking now at Eq. (40), we notice that

$$\overset{(1)}{T}=\overset{(1)}{T}_2 \tag{44}$$

and its coefficients are given by

$$\overset{(1)}{t}{}^{rs}_{\alpha\beta}=v^{rs}_{\alpha\beta}/\epsilon^{rs}_{\alpha\beta}\,. \tag{45}$$

Thus we get the familiar result

$$\Delta E^{(2)}=\tfrac{1}{4}\sum_{rs,\alpha\beta}v^{rs}_{\alpha\beta}\overset{(1)}{t}{}^{rs}_{\alpha\beta}\,. \tag{46}$$

For the calculation of $\Delta E^{(3)}$ and $\Delta E^{(4)}$, we also need $T^{(2)}$:

$$\overset{(2)}{T}\Phi=R_0([U,\overset{(1)}{T}_2]+[V,\overset{(1)}{T}_2])\Phi\,. \tag{47}$$

With the help of the contraction theorem, proven and illustrated in I, we will evaluate the commutators. We get

$$\begin{aligned}[U,\overset{(1)}{T}_2]\Phi&=-[\overset{(1)}{T}_2,U]\Phi\\&=-\sum_{rs,\alpha\beta\gamma}v^{\alpha\gamma}_{r\gamma}\overset{(1)}{t}{}^{rs}_{\alpha\beta}\Phi^{s}_{\beta}-\tfrac{1}{2}\sum_{rs\alpha\beta}\Bigg(-\sum_{\gamma\delta}v^{\gamma\delta}_{\alpha\delta}\overset{(1)}{t}{}^{rs}_{\gamma\beta}+\sum_{p\gamma}v^{r\gamma}_{p\gamma}\overset{(1)}{t}{}^{ps}_{\alpha\beta}\Bigg)\Phi^{rs}_{\alpha\beta}\,.\end{aligned} \tag{48}$$

For the second term in Eq. (47), we use

$$[V,\overset{(1)}{T}_2]\Phi=\{\underline{\overset{(1)}{T}_2V}+\underline{\underline{\overset{(1)}{T}_2V}}+\underline{\underline{\underline{\overset{(1)}{T}_2V}}}+\underline{\underline{\underline{\underline{\overset{(1)}{T}_2V}}}}\}\Phi. \tag{49}$$

Evaluation of successive contractions gives

$$\underline{\overset{(1)}{T}_2V}\Phi=-\tfrac{1}{4}\sum_{rsp,\alpha\beta\gamma}\sum_{\delta}\overset{(1)}{t}{}^{rs}_{\alpha\delta}v^{\delta p}_{\beta\gamma}\Phi^{rsp}_{\alpha\beta\gamma}+\tfrac{1}{4}\sum_{rsp,\alpha\beta\gamma}\sum_{q}\overset{(1)}{t}{}^{rq}_{\alpha\beta}v^{sp}_{q\gamma}\Phi^{rsp}_{\alpha\beta\gamma}+\tfrac{1}{2}\sum_{rs\alpha\beta}\Bigg(\sum_{p\gamma}\overset{(1)}{t}{}^{rp}_{\alpha\beta}v^{s\gamma}_{p\gamma}-\sum_{\gamma\delta}\overset{(1)}{t}{}^{rs}_{\alpha\delta}v^{\delta\gamma}_{\beta\gamma}\Bigg)\Phi^{rs}_{\alpha\beta}\,, \tag{50}$$

$$\underline{\underline{\overset{(1)}{T}_2V}}\Phi=\sum_{rs,\alpha\beta}\Bigg(\tfrac{1}{8}\sum_{pq}\overset{(1)}{t}{}^{pq}_{\alpha\beta}v^{rs}_{pq}+\tfrac{1}{8}\sum_{\gamma\delta}\overset{(1)}{t}{}^{rs}_{\gamma\delta}v^{\gamma\delta}_{\alpha\beta}-\sum_{p\gamma}\overset{(1)}{t}{}^{ps}_{\alpha\gamma}v^{r\gamma}_{p\beta}\Bigg)\Phi^{rs}_{\alpha\beta}+\sum_{r\alpha,\beta\gamma s}\overset{(1)}{t}{}^{rs}_{\alpha\beta}v^{\beta\gamma}_{s\gamma}\Phi^{r}_{\alpha}\,, \tag{51}$$

$$\underline{\underline{\underline{\overset{(1)}{T}_2V}}}\Phi=\tfrac{1}{2}\sum_{r\alpha}\Bigg(\sum_{ps,\beta}\overset{(1)}{t}{}^{ps}_{\alpha\beta}v^{r\beta}_{ps}-\sum_{\beta\gamma,s}\overset{(1)}{t}{}^{rs}_{\beta\gamma}v^{\beta\gamma}_{\alpha s}\Bigg)\Phi^{r}_{\alpha}\,, \tag{52}$$

$$\underline{\underline{\underline{\underline{\overset{(1)}{T}_2V}}}}\Phi=\tfrac{1}{4}\sum_{rs,\alpha\beta}\overset{(1)}{t}{}^{rs}_{\alpha\beta}v^{\alpha\beta}_{rs}\Phi\,. \tag{53}$$

Going back to Eq. (47), and substituting Eqs. (48)–(53), we notice the cancellation of the terms in Eq. (48) against some in Eqs. (50) and (51). We are left with

$$\overset{(2)}{T}=\overset{(2)}{T}_1+\overset{(2)}{T}_2+\overset{(2)}{T}_3\,, \tag{54}$$

indicating that $T^{(2)}$ consists of one-, two-, and three-particle cluster operators. The one-particle coefficients are found to be

$$\overset{(2)}{t}{}^{r}_{\alpha}=\langle\Phi^{r}_{\alpha}|\overset{(2)}{T}|\Phi\rangle=\frac{1}{2}\frac{1}{\epsilon^{r}_{\alpha}}\Big(\sum_{ps,\beta}\overset{(1)}{t}{}^{ps}_{\alpha\beta}v^{r\beta}_{ps}-\sum_{\beta\gamma,s}\overset{(1)}{t}{}^{rs}_{\beta\gamma}v^{\beta\gamma}_{\alpha s}\Big)\,. \tag{55}$$

Similarly we have for the two-particle coefficients

$$\overset{(2)}{t}{}^{rs}_{\alpha\beta}=\langle\Phi^{rs}_{\alpha\beta}|\overset{(2)}{T}|\Phi\rangle\,. \tag{56}$$

If we now introduce the definition

$$\overset{(2)}{\tau}{}^{rs}_{\alpha\beta}=\frac{1}{\epsilon^{rs}_{\alpha\beta}}\Big(\tfrac{1}{8}\sum_{pq}\overset{(1)}{t}{}^{pq}_{\alpha\beta}v^{rs}_{pq}+\tfrac{1}{8}\sum_{\gamma\delta}\overset{(1)}{t}{}^{rs}_{\gamma\delta}v^{\gamma\delta}_{\alpha\beta}-\sum_{p\gamma}\overset{(1)}{t}{}^{ps}_{\alpha\gamma}v^{r\gamma}_{p\beta}\Big)\,, \tag{57}$$

then Eq. (56) can be most easily represented as

$$\overset{(2)}{t}{}^{rs}_{\alpha\beta}=\sum_{r's'\alpha'\beta'}\langle\Phi^{rs}_{\alpha\beta}|\Phi^{r's'}_{\alpha'\beta'}\rangle\overset{(2)}{\tau}{}^{r's'}_{\alpha'\beta'}\,. \tag{58}$$

In this equation only four nonzero terms can arise, as $(r's')$ and $(\alpha'\beta')$ pairs can only differ by a permutation from (rs) and $(\alpha\beta)$, respectively. This causes $t^{(2)rs}_{\alpha\beta}$ to be antisymmetric in (rs) and $(\alpha\beta)$.

Finally, using the same procedure

$$\begin{aligned}\overset{(2)}{t}{}^{rsp}_{\alpha\beta\gamma}&=\langle\Phi^{rsp}_{\alpha\beta\gamma}|\overset{(2)}{T}|\Phi\rangle\\&=\sum_{r's'p',\alpha'\beta'\gamma'}\langle\Phi^{rsp}_{\alpha\beta\gamma}|\Phi^{r's'p'}_{\alpha'\beta'\gamma'}\rangle\overset{(2)}{\tau}{}^{r's'p'}_{\alpha'\beta'\gamma'}\,,\end{aligned} \tag{59}$$

with

$$\overset{(2)}{\tau}{}^{rsp}_{\alpha\beta\gamma}=\frac{1}{4}\frac{1}{\epsilon^{rsp}_{\alpha\beta\gamma}}\Big(\sum_{q}\overset{(1)}{t}{}^{rq}_{\alpha\beta}v^{sp}_{q\gamma}-\sum_{\delta}\overset{(1)}{t}{}^{rs}_{\alpha\delta}v^{\delta p}_{\beta\gamma}\Big)\,. \tag{60}$$

We are now ready to present the expression for $\Delta E^{(3)}$. From Eq. (36), and observing Eq. (44), we get

$$\Delta E^{(3)}=\langle\Phi|U\overset{(2)}{T}_1+V\overset{(2)}{T}_1+V\overset{(2)}{T}_2|\Phi\rangle\,. \tag{61}$$

The first two terms cancel, and the last term gives

$$\Delta E^{(3)}=\tfrac{1}{4}\sum_{rs,\alpha\beta}v^{\alpha\beta}_{rs}\overset{(2)}{t}{}^{rs}_{\alpha\beta}\,. \tag{62}$$

A simplification is possible for this equation. If expansion (58) is introduced, the antisymmetry property of $v^{\alpha\beta}_{rs}$ causes the same result to be obtained $2^2=4$ times. Therefore $\Delta E^{(3)}$ can also be written as

$$\Delta E^{(3)}=\sum_{rs\alpha\beta}v^{\alpha\beta}_{rs}\overset{(2)}{\tau}{}^{rs}_{\alpha\beta}\,. \tag{63}$$

Turning now to $\Delta E^{(4)}$, we start with Eq. (36). Since $T_1^{(1)}=0$, we have

$$\Delta E^{(4)}=\langle\Phi|H'\overset{(3)}{T}|\Phi\rangle\,, \tag{64}$$

which reduces to

$$\Delta E^{(4)}=\langle\Phi|U\overset{(3)}{T}_1+V\overset{(3)}{T}_1+V\overset{(3)}{T}_2|\Phi\rangle\,. \tag{65}$$

However, as in Eq. (61), the first and second terms cancel, and we are left with

$$\Delta E^{(4)}=\tfrac{1}{4}\sum_{rs\alpha\beta}v^{\alpha\beta}_{rs}\overset{(3)}{t}{}^{rs}_{\alpha\beta}\,. \tag{66}$$

This equation shows that we need only to compute the pair cluster component of $T^{(3)}$. Equation (35) gives

$$-\overset{(3)}{T}\Phi=R_0([H',\overset{(2)}{T}]+\tfrac{1}{2}[[H',\overset{(1)}{T}_2],\overset{(1)}{T}_2])\Phi\,. \tag{67}$$

The pair cluster component can be written as

$$\overset{(3)}{t}{}^{rs}_{\alpha\beta}=\langle\Phi^{rs}_{\alpha\beta}|\overset{(3)}{T}|\Phi\rangle\,. \tag{68}$$

This quantity can be extracted from Eq. (67) by considering only those contractions that can yield two particle-hole excitations. The nonzero result is

$$\begin{aligned}&\overset{(3)}{t}{}^{rs}_{\alpha\beta}\\&=\langle\Phi^{rs}_{\alpha\beta}|R_0\{\underline{\overset{(2)}{T}_1V}+\underline{\underline{\overset{(2)}{T}_2V}}+\underline{\underline{\underline{\overset{(2)}{T}_3V}}}+\tfrac{1}{2}\underline{\underline{\overset{(1)}{T}_2\,\underline{\underline{\overset{(1)}{T}_2V}}}}+\underline{\underline{\underline{\overset{(1)}{T}_2\,\underline{\overset{(1)}{T}_2V}}}}\}|\Phi\rangle.\end{aligned} \tag{69}$$

The factor (1/2) in the last multiple contraction is absent because the two asymmetrical contractions of that type are identical. Analogous to Eq. (58) we can write

$$\overset{(3)}{t}{}^{rs}_{\alpha\beta}=\sum_{r's',\alpha'\beta'}\langle\Phi^{rs}_{\alpha\beta}|\Phi^{r's'}_{\alpha'\beta'}\rangle\overset{(3)}{\tau}{}^{r's'}_{\alpha'\beta'}\,. \tag{70}$$

For clarity in presentation, we write

$$\overset{(3)}{\tau}{}^{rs}_{\alpha\beta}=\frac{1}{\epsilon^{rs}_{\alpha\beta}}(S_1+S_2+S_3+S_4+S_4'), \tag{71}$$

where S_1 to S_4' are the sums arising from the five contractions in Eq. (69). Straightforward algebra gives the result

$$S_1=\tfrac{1}{2}\Big(\sum_{u}\overset{(2)}{t}{}^{u}_{\alpha}v^{rs}_{u\beta}-\sum_{\gamma}\overset{(2)}{t}{}^{r}_{\gamma}v^{\gamma s}_{\alpha\beta}\Big), \tag{72}$$

$$S_2=\tfrac{1}{8}\sum_{pq}\overset{(2)}{t}{}^{pq}_{\alpha\beta}v^{rs}_{pq}+\tfrac{1}{8}\sum_{\gamma\delta}\overset{(2)}{t}{}^{rs}_{\gamma\delta}v^{\gamma\delta}_{\alpha\beta}-\sum_{p\gamma}\overset{(2)}{t}{}^{ps}_{\alpha\gamma}v^{r\gamma}_{p\beta}, \tag{73}$$

$$S_3=\tfrac{1}{4}\sum_{pq,\gamma}\overset{(2)}{t}{}^{rpq}_{\alpha\beta\gamma}v^{s\gamma}_{pq}-\tfrac{1}{4}\sum_{\gamma\delta,p}\overset{(2)}{t}{}^{rsp}_{\alpha\gamma\delta}v^{\gamma\delta}_{\beta p}, \tag{74}$$

$$S_4=\sum_{pq,\gamma\delta}\big(\tfrac{1}{2}\overset{(1)}{t}{}^{rp}_{\alpha\gamma}v^{\gamma\delta}_{pq}\overset{(1)}{t}{}^{qs}_{\delta\beta}+\tfrac{1}{16}\overset{(1)}{t}{}^{pq}_{\alpha\beta}v^{\gamma\delta}_{pq}\overset{(1)}{t}{}^{rs}_{\gamma\delta}\big), \tag{75}$$

$$S_4'=\tfrac{1}{4}\sum_{pq,\gamma\delta}\big(\overset{(1)}{t}{}^{pq}_{\alpha\gamma}v^{\gamma\delta}_{pq}\overset{(1)}{t}{}^{rs}_{\delta\beta}+\overset{(1)}{t}{}^{rp}_{\gamma\delta}v^{\gamma\delta}_{pq}\overset{(1)}{t}{}^{qs}_{\alpha\beta}\big). \tag{76}$$

As in the case of $\Delta E^{(3)}$, we can simplify $\Delta E^{(4)}$ to

$$\Delta E^{(4)}=\sum_{rs\alpha\beta}v^{\alpha\beta}_{rs}\overset{(3)}{\tau}{}^{rs}_{\alpha\beta}. \tag{77}$$

Equations (71) through (76), together with Eqs. (57) through (60), represent a much more compact formulation of the fourth-order correlation calculation than, for example, that given in Ref. 1. Although no computational savings arise in the evaluation of terms that involve quadruply excited states with respect to the Hartree-Fock reference Φ (i.e., our terms S_4 and S_4'), a significant reduction in the number of multiplications and additions results in the evaluation of terms involving singly, doubly, and triply, excited intermediate states (our terms S_1 through S_3). This is the consequence of the present recursive scheme. In fourth order, this reduction is relatively minor, but it will become increasingly substantial at higher orders, because the fraction of diagrams involving less-than-maximum excitations increases rapidly. The effect is more dramatic the larger the number of hole and/or particles states included.

Finally, it is worth pointing out that in the $T=T_2$ approximation (called the coupled-pair many-electron theory by Čižek[5]), the terms S_2, S_4, and S_4' are included. S_1 and S_3 are leading corrections to this approximation. The S_1 term is taken into account if the coupled-pair theory is extended to include T_1 operator.[5] The S_3 term represents then the leading (fourth-order) correction to the result obtained using such an extended coupled-pair theory.

VI. RELATION TO OTHER WORK

Most practical, finite-order perturbation calculations of correlation energy have used portions of the general scheme outlined above. For example, Bartlett and Silver,[6] and Bartlett and Shavitt[7] have summed all double excitation diagrams to finite and infinite order (the latter with Padé approximants). Their recursive scheme is equivalent to a repeated use of our Eq. (57). This approach was also used by Kvasnička and Laurinc.[8] Exploiting the $(2n+1)$ rule of perturbation theory[9] Bartlett *et al.*[6,7] could further reduce the computational effort for the calculation of double-excitation diagrammatic contributions to the correlation energy in some order. In fact, the very recent work by Kvasnička *et al.*[10] clearly shows that a systematic application of the $(2n+1)$ rule, when explicitly formulated within the coupled-cluster framework, is probably preferable in practice, because it leads to fewer arithmetic operations in any given order beyond the third one. However, until now a formal algebraic treatment is missing which would streamline the generation of the different terms as in our approach.

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