# Sixth-Order Many-Body Perturbation Theory. I. Basic Theory and Derivation of the Energy Formula

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**ABSTRACT**

The general expression for the sixth-order Møller–Plesset (MP6) energy, $E$(MP6), has been dissected in the principal part $\mathscr{A}$ and the renormalization part $\mathscr{R}$. Since $\mathscr{R}$ contains unlinked diagram contributions, which are canceled by corresponding terms of the principal part $\mathscr{A}$, $E$(MP6) has been derived solely from the linked diagram terms of the principal part $\mathscr{A}$. These have been identified by a simple procedure that starts by separating $\mathscr{A}$ into connected and disconnected cluster operator diagrams and adding terms associated with the former fully to the correlation energy. After closing all open disconnected cluster operator diagrams, one can again distinguish between connected and disconnected energy diagrams, of which only the former lead to linked diagram representations and, therefore, contributions to $E$(MP6). The connected diagram parts of $\mathscr{A}$ have been collected in four energy terms $E(\text{MP6})_1$, $E(\text{MP6})_2$, $E(\text{MP6})_3$, and $E(\text{MP6})_4$. The sum of these terms has led to an appropriate energy formula for $E$(MP6) in terms of first- and second-order cluster operators. © 1996 John Wiley & Sons, Inc.

## Introduction

Many-body perturbation theory (MBPT) in connection with the Møller–Plesset (MP) perturbation operator [1] is one of the most often used approaches to add dynamic correlation corrections to *ab initio* energies based on the Hartree–Fock (HF) approximation [2–9]. The attractiveness of MP theory results from a number of advantages. For example, MP perturbation theory offers a hierarchy of well-defined methods that provide increasing accuracy with increasing order $n$. Correlation corrections are included stepwise in a systematic way that facilitates their analysis and interpretation. At each order $n$, MP$n$ methods are size-extensive and this will also hold if parts of the MP$n$ correlation energy are considered. Since the calculation of MP correlation corrections is carried out in single, noniterative steps, the MP approach is the most economic *ab initio* method for obtaining dynamic correlation corrections. Although MBPT theory in general or MP theory in specific

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does not provide a wave function associated with a given correlation energy of order $n$, it is possible at each order $n$ to calculate molecular properties in form of response properties using analytical energy derivatives [10, 11].

As is indicated in Table I, MBPT methods are practical up to fourth-order and become more difficult to apply at higher orders. Second-order MP (MP2) theory covers double ($D$) excitations and, accordingly, describes pair correlation effects [3, 4]. At third-order MP (MP3) theory, coupling between $D$ excitations is introduced and in this way the well-known exaggeration of pair correlation effects at MP2 is partially corrected [5]. At fourth-order MP (MP4) theory, single ($S$), triple ($T$), and quadruple ($Q$) excitations are added to the $D$ excitations, thus yielding four energy contributions $E_A^{(4)}$ with $A = S$, $D$, $T$, and $Q$ which together lead to the MP4 correlation energy $E$(MP4) [6, 7]. Although the calculation of the contribution $E_Q^{(4)}$ seems to involve a cost factor of $O(M^8)$ where $M$ is the number of basis functions, a stepwise evaluation of the $Q$ term using intermediate arrays reduces the actual computational cost of calculating $E_Q^{(4)}$ to $O(M^6)$. The largest cost factor for calculating $E$(MP4) results from the evaluation of the $T$ contribution $E_T^{(4)}$ which is proportional to $O(M^7)$ (Table I).

At fifth-order MP (MP5) theory, couplings between $S$, $D$, $T$, and $Q$ excitations are introduced [8, 9]. There are 14 coupling terms $E_{AB}^{(5)}$, which because of the equivalence of terms $E_{AB}^{(5)}$ and $E_{BA}^{(5)}$ reduce to 9 unique terms (Fig. 1). Again, contributions such as $E_{QQ}^{(5)}$, the calculation of which would require $O(M^{10})$ operations in a one-step procedure, can be simplified by using intermediate arrays so that the actual cost for the determination of the MP5 correlation energy is $O(M^8)$. At MP5, a similar observation can be made as in the case of MP3: New correlation effects added in the previous (even-numbered) order are reduced by the introduction of couplings between the corresponding excitations. This happens at all odd orders of MP perturbation theory and, therefore, it can lead to an oscillatory behavior of calculated molecular properties obtained at increasing orders of perturbation theory [10, 11]. Since new excitations are not added at odd orders, odd orders of perturbation theory are mostly considered as being not very attractive for application to chemical problems. That is why MP2 and MP4 are normally used in correlation corrected *ab initio* investigations while there are relatively few studies based on either MP3 or MP5 theory.

**TABLE I**
**Description of MP$n$ methods ($n = 2, 3, \ldots, 8$).**

| Order $n$ | No. of total terms | No. of nonequivalent terms | Cost |
|---|---|---|---|
| 2 | 1 | 1 | $O(M^5)$ |
| 3 | 1 | 1 | $O(M^6)$ |
| 4 | 4 | 4 | $O(M^7)$ |
| 5 | 14 | 9 | $O(M^8)$ |
| 6 | 55 | 36 | $O(M^9)$ |
| 7 | 221 | 141 | $O(M^{10})$ |
| 8 | 915 | 583 | $O(M^{11})$ |

Although investigations using higher orders of perturbation theory ($n > 5$) have been carried out for some few-electron molecules [12, 13], there is presently no method available by which routine investigations for sixth-order MP (MP6) theory can be carried out. There are 55 energy contributions of the type $E_{ABC}^{(5)}$, which reduce to 36 because of symmetry [14]. In the upper half of Figure 1, the energy contributions $E_{ABC\ldots}^{(n)}$ at $n$th order are given in a graphical way. The rows of the diagram correspond to a given order $n$. Each energy contribution at this order $n$ corresponds to a path starting at $A = S$, $D$, $T$, or $Q$ in the row corresponding to $E_{ABC\ldots}^{(n)}$ and leading down to the bottom row, which contains the fourth-order terms $E_A^{(4)}$. For example, one obtains 14 paths at fifth-order, namely the $SS$, $SD$, $ST$, $DS$, $DD$, $DT$, $DQ$, $TS$, $TD$, $TT$, $TQ$, $QD$, $QT$, and the $QQ$ path. At sixth-order, one has to consider that $T$ and $Q$ excitations can couple with pentuple ($P$) and hextuple ($H$) excitations. Therefore, the diagram extends to the right when the paths go down to levels $n - 1$, etc. However, any allowed path can only start and end at $A = S$, $D$, $T$, $Q$, which is indicated by (wiggled) separation lines for the starting level $n$ in Figure 1.

In the lower half of Figure 1 all 55 energy paths of MP6 are listed, 19 of which are equivalent because of symmetry. Hence, there remain 36 unique paths corresponding to 36 unique energy terms $E_{ABC}^{(6)}$, which have to be calculated to determine the MP6 correlation energy.

In this and Part II of this series, we will present the basic theory and explicit formulas to carry out MP6 calculations using both algebraic and a diagrammatic approaches. The following reasons have motivated our work.

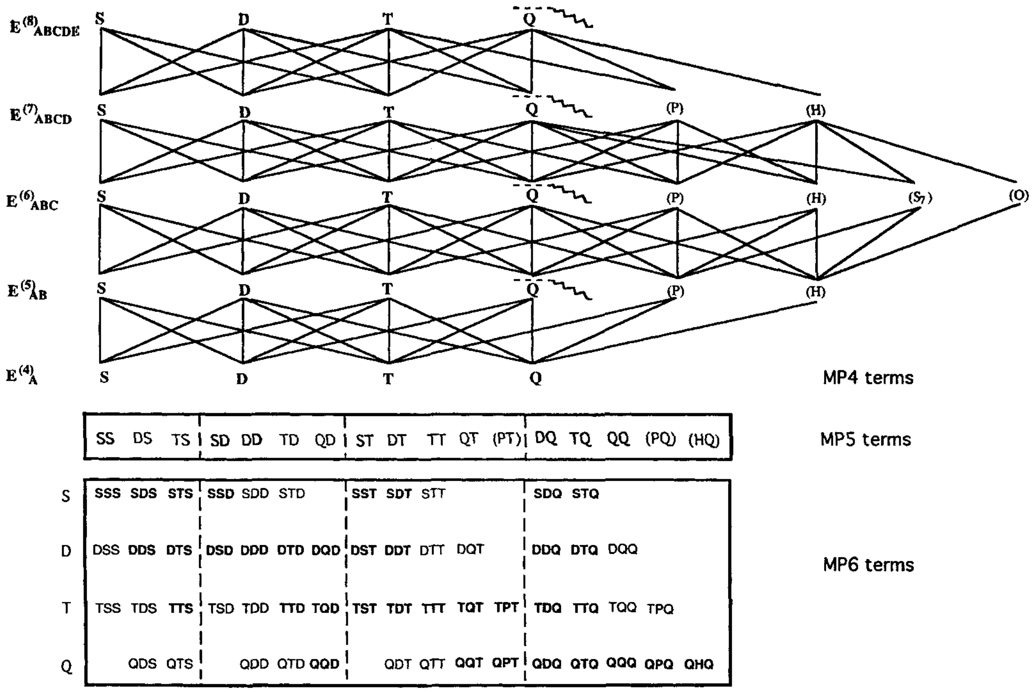



**FIGURE 1.** Graphical representation of energy contributions $E^{(n)}_{ABC\ldots}$ at $n$th order many-body perturbation theory ($n = 4, 5, 6, 7, 8$) (upper part of the figure). A particular energy contribution $E^{(n)}_{ABC\ldots}$ is given by the solid line that starts at $A = S$, $D$, $T$ or $Q$ in row $E^{(n)}$ and connects $B$, $C$, etc. at row $n-1, n-2$, etc. until $n = 4$ is reached. Note that at the $n-1, n-2, \ldots, n = 5$ level also those excitations are included that can couple with $A = S, D, T, Q$ at level $n$ and level 4 according to Slater rules. They are given in parentheses after a separator (downward directed wiggles) to the right of the $S, D, T, Q$ excitations. At the bottom of the diagram, fifth-order and sixth-order energy terms $E^{(5)}_{AB}$ and $E^{(6)}_{ABC}$, respectively, are listed in correspondence to the energy paths shown in the upper half of the diagram. Unique terms are given in bold print.

1. MP6 is after MP2 and MP4 the next even order method that should be of interest because of the introduction of new correlation effects.
2. With MP6 one has three energies (MP2, MP4, MP6) in the class of even-order methods and three in the class of odd-order methods (MP1 = HF, MP3, MP5). In this way, one gets a somewhat more realistic basis to test the convergence behavior of MP$n$ series [15].
3. Inspection of Table I and Figure 1 reveals that MP6 is actually the last method that can be developed using traditional techniques. MP7 has already a total of 221 terms, 141 of which are unique. Therefore, setting up MP7 or even higher MP$n$ methods will require some form of automated method development based on computer algebra languages.
4. The cost of a MP6 calculation is proportional to $O(M^9)$ (see Table I). This is too expensive for calculations on larger molecules, but still gives a change for systematic studies on small molecules.
5. Apart from this, there is the possibility of developing useful approximated MP6 methods, which are less costly than the full MP6 approach because they include just the more important energy contributions $E^{(6)}_{ABC}$ rather than the full set of 36 energy terms.
6. The development of MP7 and even higher MP$n$ methods becomes rather difficult (see Table I and Refs. 16 and 17) and, therefore, this work will require new techniques using computer algebra and/or modern programming languages. New programming strategies have to be developed, for which MP6 is an excellent testing ground because it represents already that degree of complication that will be encountered at all higher levels of MP$n$ theory.

In the present work, we will start from the general formulation of $n$th order perturbation theory to derive appropriate formulas for all 36 sixth-order energy terms $E^{(6)}_{ABC}$ that have to be calculated to get the MP6 correlation energy. While these terms are actually clear from the diagram shown in Figure 1, their actual evaluation has to be done in a different way in order to keep computational cost at a recent level. In the following study [18], we will present the transformation of the algebraic energy formulas into two-electron integral formulas and the structuring of a suitable computer program. We will also discuss the implementation of MP6 and present first applications of the MP6 method. Finally, in a third study [19], we will develop efficient MP6 methods that can be used in connection with MP5 and MP4 methods.

## Theory

In standard MP perturbation theory, the Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{1}$$

where $\hat{H}_0$ and $\hat{V}$ are defined by

$$\hat{H}_0 = \sum_p \hat{F}_p = \sum_p \left(\hat{h}_p + \hat{g}_p\right), \tag{2}$$

$$\hat{V} = \sum_{p<q} \hat{r}_{pq}^{-1} - \sum_p \hat{g}_p. \tag{3}$$

In Eq. (2), $\hat{h}_p$ denotes the one-electron part of the Hamiltonian and $\hat{g}_p$ covers Coulomb and exchange operators which describe two-electron interactions. The MP energy $E^{(n)}_{\mathrm{MP}} = E(\mathrm{MP}n)$ at $n$th order can be written as

$$E(\mathrm{MP}n) = \langle \Phi_0 | \hat{V} \hat{\Omega}^{(n-1)} | \Phi_0 \rangle, \tag{4}$$

where $|\Phi_0\rangle$ is the Hartree–Fock (HF) reference wave function and the wave operator $\hat{\Omega}$ at $n$th order is given by

$$\hat{\Omega}^{(n)} = \hat{G}_0 \left[ \hat{V} \hat{\Omega}^{(n-1)} - \sum_{m=1}^{n-1} E^{(m)}_{\mathrm{MP}} \hat{\Omega}^{(n-m)} \right] \tag{5}$$

with $\hat{G}_0$ being the reduced resolvent:

$$\hat{G}_0 = \sum_{k=1}^{\infty} \frac{|\Phi_k\rangle\langle\Phi_k|}{E_0 - E_k}. \tag{6}$$

In our previous work [14], we have made use of Eqs. (4) and (5) to derive the MP energy expression at sixth-order as a sum of four parts $\mathscr{A}$, $\mathscr{B}$, $\mathscr{C}$, and $\mathscr{D}$.

$$E(\mathrm{MP6}) = \mathscr{A} + \mathscr{B} + \mathscr{C} + \mathscr{D} = \mathscr{A} + \mathscr{R}. \tag{7}$$

The principal part $\mathscr{A}$ is given by Eq. (8) while parts $\mathscr{B}$, $\mathscr{C}$, and $\mathscr{D}$ given in Eqs. (9), (10), and (11) correspond to the renormalization part $\mathscr{R}$.

$$\begin{aligned}\mathscr{A} = \sum_{x_1, x_2}^{SDTQ} \sum_{y}^{SDTQPH} &\left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^{\dagger} \overline{V} \middle| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \\ &\times \overline{V}_{x_1 y} (E_0 - E_y)^{-1} \overline{V}_{y x_2} \\ &\times (E_0 - E_{x_2})^{-1} \left\langle \Phi_{x_2} \middle| \overline{V} \hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle,\end{aligned} \tag{8}$$

$$\begin{aligned}\mathscr{B} = -\sum_{d_1, d_2, d_3}^{D} \sum_{x}^{SDTQ} &V_{0d_1} (E_0 - E_{d_1})^{-1} \overline{V}_{d_1 x} \\ &\times (E_0 - E_x)^{-1} \overline{V}_{x d_2} (E_0 - E_{d_2})^{-1} V_{d_2 0} \\ &\times \left[ (E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1} + (E_0 - E_x)^{-1} \right. \\ &\left. + (E_0 - E_{d_3})^{-1} \right] V_{0 d_3} (E_0 - E_{d_3})^{-1} V_{d_3 0},\end{aligned} \tag{9}$$

$$\begin{aligned}\mathscr{C} = -\sum_{d_1, d_2}^{D} &V_{0d_1} (E_0 - E_{d_1})^{-1} \overline{V}_{d_1 d_2} (E_0 - E_{d_2})^{-1} V_{d_2 0} \\ &\times \left[ (E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1} \right] \\ &\times \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^{\dagger} \overline{V} \hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle,\end{aligned} \tag{10}$$

$$\begin{aligned}\mathscr{D} = \sum_{d_1, d_2, d_3}^{D} &V_{0d_1} (E_0 - E_{d_1})^{-1} V_{d_1 0} (E_0 - E_{d_1})^{-1} \\ &\times V_{0 d_2} (E_0 - E_{d_2})^{-1} V_{d_2 0} \\ &\times \left[ (E_0 - E_{d_1})^{-1} + (E_0 - E_{d_2})^{-1} \right] V_{0 d_3} \\ &\times (E_0 - E_{d_3})^{-1} V_{d_3 0},\end{aligned} \tag{11}$$

where $S$, $D$, $T$, $Q$, $P$, and $H$ excitations are denoted by subscripts $s$, $d$, $t$, $q$, $p$, and $h$. For general excitations $X, Y$, etc., we will use subscripts $x$, $y$, etc.

In Eqs. (8)–(11) the following terms have been used:

$$V_{0d} = \langle \Phi_0 | \hat{V} | \Phi_d \rangle, \tag{12}$$

$$\overline{V}_{xy} = \langle \Phi_x | \hat{V} | \Phi_y \rangle - \delta_{xy} \langle \Phi_0 | \hat{V} | \Phi_0 \rangle, \tag{13}$$

and

$$\hat{T}_2^{(1)}|\Phi_0\rangle = \sum_d^D |\Phi_d\rangle (E_0 - E_d)^{-1} V_{d0}. \qquad (14)$$

Energies $E_0$, $E_d$, $E_x$, and $E_y$ of Eqs. (8)–(14) are eigenvalues of the unperturbed Hamiltonian $\hat{H}_0$ corresponding to the eigenfunctions $|\Phi_0\rangle$, $|\Phi_d\rangle$ (doubly excited), $|\Phi_x\rangle$ ($x$-fold excited), and $|\Phi_y\rangle$ ($y$-fold excited). Operator $\hat{T}_2^{(1)}$ is the double excitation cluster operator at first-order perturbation theory. At second-order perturbation theory, there are the single, double, and triple excitation cluster operators $\hat{T}_1^{(2)}$, $\hat{T}_2^{(2)}$ and $\hat{T}_3^{(2)}$, respectively:

$$\hat{T}_1^{(2)}|\Phi_0\rangle = \sum_s^S |\Phi_s\rangle (E_0 - E_s)^{-1} \langle \Phi_s|\overline{V}\hat{T}_2^{(1)}|\Phi_0\rangle, \qquad (15)$$

$$\hat{T}_2^{(2)}|\Phi_0\rangle = \sum_d^D |\Phi_d\rangle (E_0 - E_d)^{-1} \langle \Phi_d|\overline{V}\hat{T}_2^{(1)}|\Phi_0\rangle, \qquad (16)$$

$$\hat{T}_3^{(2)}|\Phi_0\rangle = \sum_t^T |\Phi_t\rangle (E_0 - E_t)^{-1} \langle \Phi_t|\overline{V}\hat{T}_2^{(1)}|\Phi_0\rangle, \qquad (17)$$

which will be used in the derivation of $E$(MP6).

The renormalization term $\mathscr{R} = \mathscr{B} + \mathscr{C} + \mathscr{D}$ contains unlinked diagram contributions. According to the linked diagram theorem [20], the unlinked diagram terms of Eqs. (9)–(11) must be canceled by corresponding terms of the principal part $\mathscr{A}$ in order to guarantee proper dependence of the energy $E$(MP6) on the size of the system (size extensivity [21]). Accordingly, only the linked diagram terms of part $\mathscr{A}$ contribute to $E$(MP6) in its final form.

Since unlinked diagram terms contain disconnected closed parts in their graphical representation, a convenient way of distinguishing between linked and unlinked diagram terms of the principal part $\mathscr{A}$ is to check whether a given term $\mathscr{A}(X_1, Y, X_2)$:

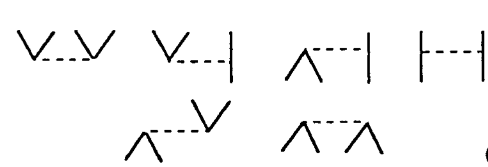
$$\begin{aligned}\mathscr{A}(X_1, Y, X_2) &= \sum_{x_1, x_2}^{X_1, X_2} \sum_y^Y \left\langle \Phi_0 \left| \left(\hat{T}_2^{(1)}\right)^{\dagger} \overline{V} \right| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \\ &\quad \times \overline{V}_{x_1 y} (E_0 - E_y)^{-1} \overline{V}_{y x_2} \\ &\quad \times (E_0 - E_{x_2})^{-1} \left\langle \Phi_{x_2} \left| \overline{V}\hat{T}_2^{(1)} \right| \Phi_0 \right\rangle\end{aligned}$$

$$(X_1, X_2 = S, D, T, Q; Y = S, D, T, Q, P, H) \qquad (18)$$

contains disconnected cluster operator parts in its graphical representation. For example, for $X_1$, $X_2 = S, D, T$ and $Y = S, D$, the diagrammatic representations of $\mathscr{A}(X_1, Y, X_2)$ can only contain connected diagram parts and therefore, the corresponding terms represent linked diagram contributions, which fully contribute to the energy $E$(MP6). In such a case, we call the whole term $\mathscr{A}(X_1, Y, X_2)$ a connected cluster operator diagram term. For example, the terms $\mathscr{A}(X_1, T, X_2)$ ($X_1$, $X_2 = D, T$) and $\mathscr{A}(T, Q, T)$ are also associated with connected cluster operator diagram terms. But for $X_2 = Q$, $\mathscr{A}(X_1, Y, Q)$ can be written as

$$\begin{aligned}\mathscr{A}(X_1, Y, Q) &= \sum_{x_1}^{X_1} \sum_y^Y \sum_q^Q \left\langle \Phi_0 \left| \left(\hat{T}_2^{(1)}\right)^{\dagger} \overline{V} \right| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \\ &\quad \times \overline{V}_{x_1 y} (E_0 - E_y)^{-1} \overline{V}_{yq} \\ &\quad \times (E_0 - E_q)^{-1} \left\langle \Phi_q \left| \overline{V}\hat{T}_2^{(1)} \right| \Phi_0 \right\rangle \\ &= \sum_{x_1}^{X_1} \sum_y^Y \left\langle \Phi_0 \left| \left(\hat{T}_2^{(1)}\right)^{\dagger} \overline{V} \right| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \\ &\quad \times \overline{V}_{x_1 y} (E_0 - E_y)^{-1} \left\langle \Phi_y \left| \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right| \Phi_0 \right\rangle,\end{aligned} \qquad (19)$$

where a disconnected cluster operator $\frac{1}{2}(\hat{T}_2^{(1)})^2$ appears, which corresponds to a disconnected diagram part in the graphical representation of $\mathscr{A}(X_1, Y, Q)$ and, accordingly, leads to linked and unlinked diagram contributions to the energy. Thereby, $\mathscr{A}(X_1, Y, Q)$, contrary to the connected cluster operator diagram terms $\mathscr{A}(X_1, Y, X_2)$ ($X_1$, $X_2 = S, D, T, Y = S, D$, etc.), contributes only partially to $E$(MP6). In this case, we call the whole term a disconnected cluster operator diagram term because of the presence of disconnected diagram parts in the graphical representation. The other terms of principal part $\mathscr{A}$ all involve disconnected cluster operator diagrams. In order to show this, we introduce graphical representations of perturbation operator $\overline{V}$ and cluster operators $\hat{T}_i^{(n)}$ ($i = 1, 2, 3$) at $n$th order perturbation theory, taking the HF wave function $|\Phi_0\rangle$ as a reference function,

$\hat{V}$:  (20)

$\hat{T}_1^{(n)}$:  (21)

$\hat{T}_2^{(n)}$:  (22)

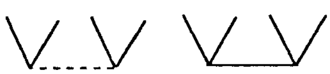
$\hat{T}_3^{(n)}$:  (23)

In Eqs. (20)–(23) as well as in the following equations, diagrams are given in a simplified form since they will only be used to distinguish between linked and unlinked diagram terms. In terms of Eq. (22) one can express the cluster operator $\frac{1}{2}(\hat{T}_2^{(1)})^2$ in a diagrammatic form shown in Eq. (24).

$\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2$:  (24)

Using Eqs. (20)–(23) one can identify other disconnected diagram parts resulting from products of the operator $\overline{V}$ and the cluster operators $\hat{T}_i^{(2)}$ ($i = 1, 2, 3$):

$|\Phi_t\rangle\langle\Phi_t|\overline{V}\hat{T}_1^{(2)}|\Phi_0\rangle$:  (25)

$|\Phi_q\rangle\langle\Phi_q|\overline{V}\hat{T}_2^{(2)}|\Phi_0\rangle$:  (26)

$|\Phi_p\rangle\langle\Phi_p|\overline{V}\hat{T}_3^{(2)}|\Phi_0\rangle$:  (27)

which appear in the terms $\mathscr{A}(X_1, T, S)$, $\mathscr{A}(X_1, Q, D)$, and $\mathscr{A}(X_1, P, T)$, respectively. All disconnected diagram terms are found in these terms as well as in $\mathscr{A}(X_1, Y, Q)$.

In summary, all terms of the principal part $\mathscr{A}$ can be identified as being associated with connected or disconnected cluster operator diagrams. The latter can be further categorized by distinguishing between disconnected diagram parts associated with $T$, $Q$, or $P$ excitations. Accordingly, we dissect all terms associated with the disconnected cluster operator diagrams of $\mathscr{A}$ into three parts. The first part covers $Q$ contributions given in Eqs. (24) and (26), namely $\mathscr{A}(X_1, Y, Q)$ and $\mathscr{A}(X_1, Q, D)$. The second and the third part correspond to $T$ and $P$ contributions given by Eqs. (25) and (27), namely $\mathscr{A}(X_1, T, S)$ and $\mathscr{A}(X_1, P, T)$.

A simple procedure is applied to identify all linked diagram (LD) contributions to the correlation energy $E$(MP6). No matter whether a given diagram represents a wave operator or energy part of $\mathscr{A}$, a connected diagram always leads to a linked energy diagram and, therefore, a contribution to the correlation energy. The disconnected diagrams can be open wave operator or closed energy diagrams, which upon closure of the former can be all grouped into connected or disconnected energy diagrams. Again, only the former represent LD terms, which have to be added to the correlation energy. In this way, all LD terms are identified and the calculation of $E(\text{MP6}) = \mathscr{A}_{\text{LD}}$ is possible.

In setting up the expression for $E$(MP6) one has to realize that under certain circumstances simplifications are possible when parts of $\mathscr{A}$ are calculated at the same time. For example, parts of $\mathscr{A}(X_1, Y, Q)$ ($Y = T, Q, P$) can be combined with $\mathscr{A}(X_1, T, S)$, $\mathscr{A}(X_1, Q, D)$ and $\mathscr{A}(X_1, P, T)$ thus leading to a reduction of the corresponding computational cost as will be discussed below. Therefore, it is useful to analyze the term $\mathscr{A}(X_1, Y, Q)$ by diagrammatic techniques before focusing on $\mathscr{A}(X_1, T, S)$, $\mathscr{A}(X_1, Q, D)$, and $\mathscr{A}(X_1, P, T)$.

In the following, we will derive explicit expressions for the LD terms of $\mathscr{A}$ in form of the 36 energy contributions $E_{ABC}^{(6)}$ with $A, B, C = S, D, T, Q, P, H$. We will give each energy contribution in a cluster operator form, which can easily be converted into two-electron integral forms [18]. For this purpose, sixth-order energy $E(\text{MP6}) = \mathscr{A}_{\text{LD}}$ will be split into four parts $E(\text{MP6})_1$, $E(\text{MP6})_2$, $E(\text{MP6})_3$ and $E(\text{MP6})_4$, respectively, following the analysis of the principal part $\mathscr{A}$ in terms of connected and disconnected cluster operator diagram contributions. $E(\text{MP6})_1$ contains 16 energy terms $E_{ABC}^{(6)}$ corresponding to connected cluster operator diagram terms. $E(\text{MP6})_2$ also covers 16 energy terms which result from disconnected $Q$ cluster operators. The remaining four terms are given by $E(\text{MP6})_3$ and $E(\text{MP6})_4$ which correspond to $\mathscr{A}(X_1, T, S)$ (three $T$ contributions) and $\mathscr{A}(X_1, P, T)$ (one $P$ contribution), respectively. Explicit formulas for $E(\text{MP6})_1$, $E(\text{MP6})_2$, $E(\text{MP6})_3$ and $E(\text{MP6})_4$ will be derived in the following sections.

## DERIVATION OF $E(\text{MP6})_{1a}$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = S, D, T$; $Y = S, D$; $X_2 = S, D, T$

In this case, Eq. (8) does not contain any unlinked diagram terms and, accordingly, it is straightforward to express $E(\mathrm{MP6})_{1a}$ by

$$E(\mathrm{MP6})_{1a} = \sum_{i,j}^{1,2,3} \sum_{y}^{SD} \left\langle \Phi_0 \middle| \left(\hat{T}_i^{(2)}\right)^{\dagger} \bar{V} \middle| \Phi_y \right\rangle \times (E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \bar{V}\hat{T}_j^{(2)} \middle| \Phi_0 \right\rangle$$
$$= E_{SSS}^{(6)} + 2E_{SSD}^{(6)} + 2E_{SST}^{(6)} + E_{SDS}^{(6)} + 2E_{SDD}^{(6)} + 2E_{SDT}^{(6)} + E_{DSD}^{(6)} + 2E_{DST}^{(6)} + E_{DDD}^{(6)} + 2E_{DDT}^{(6)} + E_{TST}^{(6)} + E_{TDT}^{(6)}. \quad (28)$$

Note that $E_{SSD}^{(6)} = E_{DSS}^{(6)}$, etc., which leads to a reduction from 18 to 12 terms $E_{ABC}^{(6)}$ in Eq. (28), which have to be weighted by appropriate factors of 1 or 2.

## DERIVATION OF $E(\mathrm{MP6})_{1b}$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = D, T$, $Y = T$, $X_2 = D, T$; $X_1 = T$, $Y = Q$, $X_2 = T$

Again, the principal part $\mathscr{A}(X_1, Y, X_2)$ contains just linked diagram terms, which lead to four energy contributions $E_{ABC}^{(6)}$ covering $T$ effects:

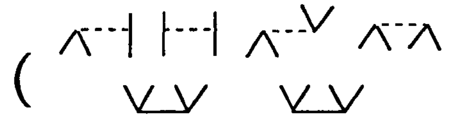
$$E(\mathrm{MP6})_{1b} = \sum_{i,j}^{2,3} \sum_{t}^{T} \left\langle \Phi_0 \middle| \left(\hat{T}_i^{(2)}\right)^{\dagger} \bar{V} \middle| \Phi_t \right\rangle (E_0 - E_t)^{-1} \times \left\langle \Phi_t \middle| \bar{V}\hat{T}_j^{(2)} \middle| \Phi_0 \right\rangle + \sum_{q}^{Q} \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^{\dagger} \bar{V} \middle| \Phi_q \right\rangle \times (E_0 - E_q)^{-1} \left\langle \Phi_q \middle| \bar{V}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle$$
$$= E_{DTD}^{(6)} + 2E_{DTT}^{(6)} + E_{TTT}^{(6)} + E_{TQT}^{(6)}. \quad (29)$$

Hence, $E(\mathrm{MP6})_1 = E(\mathrm{MP6})_{1a} + E(\mathrm{MP6})_{1b}$ covers in total 16 energy terms, for which explicit formulas are given in Eqs. (A1)–(A16) of the Appendix. In none of these 16 cases is it possible to further simply the corresponding energy expressions and to reduce computational cost when evaluating them. This, however, is different for the following energy contribution $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$.

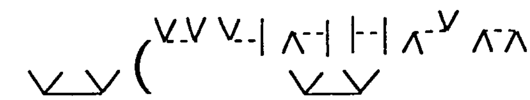
## DERIVATION OF $E(\mathrm{MP6})_{2a}$ FROM $\mathscr{A}(X_1, Y, Q)$ WITH $X_1 = S, D, T, Q$; $Y = D, T, Q, P, H$; $X_2 = Q$

$\mathscr{A}(X_1, Y, Q)$ is given by Eq. (19), in which the $Q$ effects can be diagrammatically described by the connected part $\langle \Phi_y | [\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_C | \Phi_0 \rangle$ and the disconnected part $\langle \Phi_y | [\hat{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_D | \Phi_0 \rangle$:

$|\Phi_y\rangle \left\langle \Phi_y \middle| \left[ \bar{V}\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle$:


(30)

$|\Phi_y\rangle \left\langle \Phi_y \middle| \left[ \bar{V}\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle$:


(31)

where subscript $C$ (or $D$) indicates limitation to "connected" (or "disconnected") cluster operator diagrams so that $\mathscr{A}(X_1, Y, Q)$ can also be separated into $\mathscr{A}(X_1, Y, Q_C)$ and $\mathscr{A}(X_1, Y, Q_D)$:

$$\mathscr{A}(X_1, Y, Q_C) = \sum_{x_1}^{X_1} \sum_{y}^{Y} \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^{\dagger} \bar{V} \middle| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \times \bar{V}_{x_1 y}(E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \left[ \bar{V}\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle, \quad (32)$$

$$\mathscr{A}(X_1, Y, Q_D) = \sum_{x_1}^{X_1} \sum_{y}^{Y} \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^{\dagger} \bar{V} \middle| \Phi_{x_1} \right\rangle (E_0 - E_{x_1})^{-1} \times \bar{V}_{x_1 y}(E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \left[ \bar{V}\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle. \quad (33)$$

Equations (32) and (33) cover for $X_1 = Q$ four possibilities, namely $\mathscr{A}(Q_C, Y, Q_C)$, $\mathscr{A}(Q_D, Y, Q_C)$, $\mathscr{A}(Q_C, Y, Q_D)$, and $\mathscr{A}(Q_D, Y, Q_D)$. The first term contains just linked diagram terms, while the last term and the remaining terms $\mathscr{A}(Q_D, Y, Q_C) = \mathscr{A}(Q_C, Y, Q_D)$ can cover linked and/or unlinked diagrams, which has to be investigated in each case. For convenience, we split $E(\mathrm{MP6})_{2a}$ into three parts: (1) $Y = D$, (2) $Y = T, Q, P$, and (3) $Y = H$, which are discussed in the following.

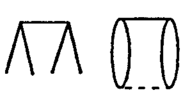
## DERIVATION OF $E(\mathrm{MP6})_{2a_1}$ FROM $\mathscr{A}(X_1, Y, Q)$ WITH $X_1 = S, D, T, Q$; $Y = D$; $X_2 = Q$

When $Y$ runs over all $D$ excitations in Eq. (32), the first three terms in $\mathscr{A}(X_1, D, Q_C)$ correspond to connected, closed (linked) diagrams leading to the energy contributions $E^{(6)}_{SDQ}$, $E^{(6)}_{DDQ}$, and $E^{(6)}_{TDQ}$. For $X_1 = Q$, $\mathscr{A}(Q_C, D, Q_C)$ represents a linked diagram part, which is equal to $E^{(6)}_{QDQ}$. If, however, either Eq. (32) or (33) contains a disconnected part such as $\{\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\overline{V}\}_D$:

$$\mathscr{A}(Q_D, D, Q_C) = \sum_d^D \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[ \left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \overline{V} \right\}_D \middle| \Phi_d \right\rangle \times (E_0 - E_d)^{-1} \left\langle \Phi_d \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle \quad (34)$$

then, this will lead to an unlinked diagram contribution as can be seen from Eq. (35):

$$\left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[ \left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \overline{V} \right\}_D \middle| \Phi_d \right\rangle \langle \Phi_d |:$$



(35)

This means that all possible contributions from $\mathscr{A}(X_1, D, Q_D)$ with $X_1 = S, D, T, Q$ correspond to unlinked diagrams, which can be disregarded. Hence, there is no contribution from $\mathscr{A}(X_1, D, Q_D)$ to $E(\mathrm{MP6})$ and, accordingly, $E(\mathrm{MP6})_{2a_1}$ is given by

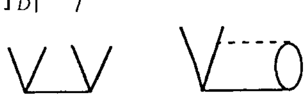
$$E(\mathrm{MP6})_{2a_1} = 2E^{(6)}_{SDQ} + 2E^{(6)}_{DDQ} + 2E^{(6)}_{TDQ} + E^{(6)}_{QDQ}. \quad (36)$$

Explicit expressions for the energy contributions of Eq. (36) are given in Eqs. (A17)–(A20) of the Appendix.

## DERIVATION OF $E(\mathrm{MP6})_{2a_2}$ FROM $\mathscr{A}(X_1, Y, Q)$ WITH $X_1 = S, D, T, Q$; $Y = T, Q, P$; $X_2 = Q$

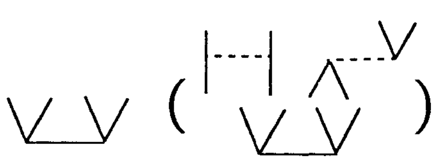
In this case, the term $\langle \Phi_y | [\overline{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_D | \Phi_0 \rangle$ ($y = t, q, p$) in Eq. (33) represents disconnected, open-diagram parts:

$$|\Phi_t\rangle \left\langle \Phi_t \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle:$$



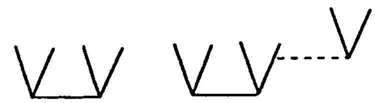
(37)

$$|\Phi_q\rangle \left\langle \Phi_q \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle:$$



(38)

$$|\Phi_p\rangle \left\langle \Phi_p \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle:$$



(39)

The term $\mathscr{A}(X_1, Y, Q_D)$ contains both linked and unlinked diagrams, where the former lead to partial energy contributions $E^{(6)}_{X_1YQ}(\mathrm{I})$. Because of computational considerations, it is advisable to evaluate contributions $E^{(6)}_{X_1YQ}(\mathrm{I})$ in connection with energy terms $E^{(6)}_{X_1TS}$ [$E(\mathrm{MP6})_3$], $E^{(6)}_{X_1QD}$ [$E(\mathrm{MP6})_{2b}$], and $E^{(6)}_{X_1PT}$ [$E(\mathrm{MP6})_4$]. The complementary energy contributions $E^{(6)}_{X_1YQ}(\mathrm{II})$ [$E^{(6)}_{X_1YQ} = E^{(6)}_{X_1YQ}(\mathrm{I}) + E^{(6)}_{X_1YQ}(\mathrm{II})$] are contained in $\mathscr{A}(X_1, Y, Q_C)$ of Eq. (32), which includes for $Y = T$ or $Q$ just linked diagrams. The case $Y = P$ can be excluded since $\mathscr{A}(X_1, P, Q_C)$ does not contribute to $E(\mathrm{MP6})$. This can be seen if one has the operator $[\overline{V}\frac{1}{2}(\hat{T}_2)^2]_C$ acting on the reference wave function $|\Phi_0\rangle$: It is impossible to generate $p$-fold excited wave functions $|\Phi_p\rangle$.

The term $\mathscr{A}(X_1, Y, Q_C)$ covers seven partial energy contributions, which are summarized in $E(\mathrm{MP6})_{2a_2}$ according to

$$E(\mathrm{MP6})_{2a_2} = \sum_X^{SDTQ} E^{(6)}_{XTQ}(\mathrm{II}) + \sum_X^{DTQ} E^{(6)}_{XQQ}(\mathrm{II}). \quad (40)$$

The computation of $E^{(6)}_{STQ}(\mathrm{II})$ and $E^{(6)}_{DQQ}(\mathrm{II})$ can be simplified by splitting $E^{(6)}_{QTQ}(\mathrm{II})$ and $E^{(6)}_{QQQ}(\mathrm{II})$ in two parts $\mathrm{II}_a$ and $\mathrm{II}_b$ according to Eqs. (41)–(42), and combining part $\mathrm{II}_a$ with $E^{(6)}_{STQ}(\mathrm{II})$ and $E^{(6)}_{DQQ}(\mathrm{II})$.

$$E^{(6)}_{QYQ}(\mathrm{II})_a = \sum_y^Y \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[ \left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \overline{V} \right\}_D \middle| \Phi_y \right\rangle \times (E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle, \quad (41)$$

$$E^{(6)}_{QYQ}(\mathrm{II})_b = \sum_y^Y \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[ \left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \overline{V} \right\}_C \middle| \Phi_y \right\rangle \times (E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \left[ \overline{V} \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle$$
$$(Y = T, Q). \quad (42)$$

Utilizing the factorization theorem [22], namely $(xy)^{-1} = (x + y)^{-1}(x^{-1} + y^{-1})$, Eq. (43) can be simplified to Eq. (44):

$$E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a$$
$$= \sum_t^T \Bigg[ \left\langle \Phi_0 \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \bar{V} \middle| \Phi_t \right\rangle + \left\langle \Phi_0 \middle| \left(\tfrac{1}{2}\left(\left(\hat{T}_2^{(1)}\right)^\dagger\right)^2 \bar{V}\right)_D \middle| \Phi_t \right\rangle \Bigg] \times (E_0 - E_t)^{-1} \left\langle \Phi_t \middle| \left(\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right)_C \middle| \Phi_0 \right\rangle \quad (43)$$
$$= \left\langle \Phi_0 \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \left(\hat{T}_2^{(1)}\right)^\dagger \left(\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right)_C \middle| \Phi_0 \right\rangle. \quad (44)$$

This is done by rewriting the bracket part of Eq. (43) according to Eqs. (45a) and (45b):

$$\left\langle \Phi_0 \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \bar{V} \middle| \Phi_t \right\rangle + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\left(\hat{T}_2^{(1)}\right)^\dagger\right)^2 \bar{V}\right]_D \middle| \Phi_t \right\rangle$$
$$= \left\langle \Phi_0 \middle| \bar{V}\left(\hat{T}_1^{(2)}\right)^\dagger \middle| \Phi_t \right\rangle + \left\langle \Phi_0 \middle| \left[\left(\hat{T}_2^{(1)}\right)^\dagger \bar{V}\right]_C \left(\hat{T}_2^{(1)}\right)^\dagger \middle| \Phi_t \right\rangle \quad (45a)$$
$$= \sum_d^D \langle \Phi_0 | \bar{V} | \Phi_d \rangle \left\langle \Phi_d \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \middle| \Phi_t \right\rangle + \sum_s^S \left\langle \Phi_0 \middle| \left[\left(\hat{T}_2^{(1)}\right)^\dagger \bar{V}\right]_C \middle| \Phi_s \right\rangle \left\langle \Phi_s \middle| \left(\hat{T}_2^{(1)}\right)^\dagger \middle| \Phi_t \right\rangle$$
$$= \sum_d^D \sum_s^S \langle \Phi_0 | \bar{V} | \Phi_d \rangle \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^\dagger \bar{V} \middle| \Phi_s \right\rangle \times \Big[ (E_0 - E_s)^{-1} \langle \Phi_d | \hat{t}_s^\dagger | \Phi_t \rangle + (E_0 - E_d)^{-1} \langle \Phi_s | \hat{t}_d^\dagger | \Phi_t \rangle \Big]$$
$$= \left\langle \Phi_0 \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \left(\hat{T}_2^{(1)}\right)^\dagger \bar{V} \middle| \Phi_t \right\rangle (E_0 - E_t), \quad (45b)$$

where $\hat{t}_s$ and $\hat{t}_d$ denote elementary singles and doubles substitution operators (e.g., $\hat{t}_s|\Phi_0\rangle = |\Phi_s\rangle$ and $\hat{t}_d|\Phi_0\rangle = |\Phi_d\rangle$) and the following identity has been used in Eq. (45) [23]:

$$\left\langle \Phi_y \middle| \left(\bar{V}\hat{T}_m\hat{T}_n\right)_D \middle| \Phi_0 \right\rangle = \left\langle \Phi_y \middle| \hat{T}_m\left(\bar{V}\hat{T}_n\right)_C \middle| \Phi_0 \right\rangle + \left\langle \Phi_y \middle| \hat{T}_n\left(\bar{V}\hat{T}_m\right)_C \middle| \Phi_0 \right\rangle. \quad (46)$$

In a similar way we can derive the sum $E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$:

$$E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$$
$$= \sum_q^Q \Bigg[ \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(2)}\right)^\dagger \bar{V} \middle| \Phi_q \right\rangle + \left\langle \Phi_0 \middle| \left\{\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \bar{V}\right\}_D \middle| \Phi_q \right\rangle \Bigg] \times (E_0 - E_q)^{-1} \left\langle \Phi_q \middle| \left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C \middle| \Phi_0 \right\rangle \quad (47a)$$
$$= \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(2)}\right)^\dagger \left(\hat{T}_2^{(1)}\right)^\dagger \left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C \middle| \Phi_0 \right\rangle. \quad (47b)$$

Since the energy denominators in Eqs. (43) and (47a) involve $T$ and $Q$ energies, respectively, their calculation requires $O(M^7)$ and $O(M^9)$ steps. By rewriting (43) and (47a) according to (44) and (47b) and eliminating the $T$ and $Q$ energy denominators, the cost for calculating $E_{STQ}^{(6)}(\mathrm{II})$ and $E_{DQQ}^{(6)}(\mathrm{II})$ is reduced to $O(M^6)$. In view of this, it is advisable to eliminate $T, Q, P, H$ energy denominators in the expression for principal part $\mathscr{A}$ [Eq. (8)].

The total contribution of the connected part $\mathscr{A}(X_1, Y, Q_C)$ [Eq. (40)] to $E(\mathrm{MP6})$ is given by

$$E(\mathrm{MP6})_{2a_2} = \left[E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a\right] + E_{QTQ}^{(6)}(\mathrm{II})_b + \left[E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a\right] + E_{QQQ}^{(6)}(\mathrm{II})_b + 2E_{DTQ}^{(6)}(\mathrm{II}) + 2E_{TTQ}^{(6)}(\mathrm{II}) + 2E_{TQQ}^{(6)}(\mathrm{II}) \quad (48)$$

where symmetric terms are covered by a factor of 2 in the case of $E_{DTQ}^{(6)}(\mathrm{II}) = E_{QTD}^{(6)}(\mathrm{II})$, $E_{TTQ}^{(6)}(\mathrm{II})$, and $E_{TQQ}^{(6)}(\mathrm{II})$. Explicit expressions for $E_{QTQ}^{(6)}(\mathrm{II})_b$, $E_{QQQ}^{(6)}(\mathrm{II})_b$ $E_{DTQ}^{(6)}(\mathrm{II})$, $E_{TTQ}^{(6)}(\mathrm{II})$, and $E_{TQQ}^{(6)}(\mathrm{II})$ are given in Eqs. (A23), (A30), (A26), (A32), and (A34) of the Appendix.

## DERIVATION OF $E(\mathrm{MP6})_{2a_3}$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = Q$; $Y = H$; $X_2 = Q$

When setting $Y = H$ in Eq. (19), the connected part of $\mathscr{A}$ leads to the energy term $E_{QHQ}^{(6)}$, which can be developed in the following way:

$$\mathscr{A}(Q, H, Q) = \sum_h^H \left\langle \Phi_0 \middle| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \bar{V} \middle| \Phi_h \right\rangle \times (E_0 - E_h)^{-1} \left\langle \Phi_h \middle| \bar{V}\frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \middle| \Phi_0 \right\rangle$$
$$= \left\langle \Phi_0 \middle| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \bar{V}\frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3 \middle| \Phi_0 \right\rangle. \quad (49)$$

By utilizing the identity (factorization theorem) [22]:

$$\frac{1}{xyz} = \frac{1}{x+y+z}\left(\frac{1}{xy} + \frac{1}{xz} + \frac{1}{yz}\right)$$

the connected part of $\mathscr{A}(Q, H, Q)$ simplifies to

$$\begin{aligned}
E(\mathrm{MP6})_{2a_3} &= E_{QHQ}^{(6)} \\
&= \left\langle \Phi_0 \left| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V} \frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3 \right| \Phi_0 \right\rangle_C \\
&= \left\langle \Phi_0 \left| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left[\overline{V} \frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3\right]_D \right| \Phi_0 \right\rangle_C \\
&\quad + \left\langle \Phi_0 \left| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left[\overline{V} \frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3\right]_C \right| \Phi_0 \right\rangle \\
&= \left\langle \Phi_0 \left| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \hat{T}_2^{(1)} \left[\overline{V} \frac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C \right| \Phi_0 \right\rangle_C \\
&\quad + \left\langle \Phi_0 \left| \frac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left[\overline{V} \frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3\right]_C \right| \Phi_0 \right\rangle.
\end{aligned} \tag{50}$$

Using a series of intermediate arrays, evaluation of the two terms of Eq. (50) requires just $O(M^6)$ computational steps so that the calculation of $E_{QHQ}^{(6)}$ is not very time demanding in an MP6 energy computation.

## DERIVATION OF $E(\mathrm{MP6})_{2b}$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = D, T, Q$; $Y = Q$; $X_2 = D$

After discussing $Q$ contributions already in connection with $E(\mathrm{MP6})_{1b}$ and $E(\mathrm{MP6})_{2a}$, there remain just three $Q$ terms resulting from $\mathscr{A}(X_1, Q, D)$ with $X_1 = D, T, Q$.

$$\begin{aligned}
\sum_{X_1}^{D,T,Q} \mathscr{A}(X_1, Q, D) &= \sum_i^{2,3} \sum_q^{Q} (2 - \delta_{i,2}) \left\langle \Phi_0 \left| \left(\hat{T}_i^{(2)}\right)^\dagger \overline{V} \right| \Phi_q \right\rangle \\
&\quad \times (E_0 - E_q)^{-1} \left\langle \Phi_q \left| \overline{V} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle \\
&\quad + \sum_q^{Q} \left\langle \Phi_0 \left| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V} \right| \Phi_q \right\rangle \\
&\quad \times (E_0 - E_q)^{-1} \left\langle \Phi_q \left| \overline{V} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle.
\end{aligned} \tag{51}$$

It is of computational advantage to combine the first term of Eq. (51), $\mathscr{A}(D, Q, D)$, with $\mathscr{A}(D, Q, Q_D)$ of Eq. (33) ($X_1 = D, Y = Q$) using the same approach as discussed in connection with Eq. (47). This leads to

$$\begin{aligned}
\mathscr{A}(D, Q, D) + \mathscr{A}(D, Q, Q_D) &= \sum_q^{Q} \left\langle \Phi_0 \left| \left(\hat{T}_2^{(2)}\right)^\dagger \overline{V} \right| \Phi_q \right\rangle (E_0 - E_q)^{-1} \\
&\quad \times \left\{ \left\langle \Phi_q \left| \overline{V} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle \right. \\
&\quad \left. + \left\langle \Phi_q \left| \left[\overline{V} \tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_D \right| \Phi_0 \right\rangle \right\} \\
&= \left\langle \Phi_0 \left| \left(\hat{T}_2^{(2)}\right)^\dagger \overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle,
\end{aligned} \tag{52}$$

which contributes to $E(\mathrm{MP6})$ (by its connected part) the two energy terms $E_{DQD}^{(6)}$ and $E_{DQQ}^{(6)}(\mathrm{I})$:

$$\begin{aligned}
E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \left| \left(\hat{T}_2^{(2)}\right)^\dagger \overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle_C \\
&= \left\langle \Phi_0 \left| \left(\hat{T}_2^{(2)}\right)^\dagger \left(\overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)}\right)_C \right| \Phi_0 \right\rangle.
\end{aligned} \tag{53}$$

Analogously, the combination of $\mathscr{A}(T, Q, D)$ [$X_1 = T$ in Eq. (51)] with $\mathscr{A}(T, Q, Q_D)$ defined by Eq. (33) leads to

$$\begin{aligned}
\mathscr{A}(T, Q, D) + \mathscr{A}(T, Q, Q_D) &= 2\sum_q^{Q} \left\langle \Phi_0 \left| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V} \right| \Phi_q \right\rangle (E_0 - E_q)^{-1} \\
&\quad \times \left[ \left\langle \Phi_q \left| \overline{V} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle \right. \\
&\quad \left. + \left\langle \Phi_q \left| \left[\overline{V} \tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_D \right| \Phi_0 \right\rangle \right] \\
&= 2\left\langle \Phi_0 \left| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)} \right| \Phi_0 \right\rangle.
\end{aligned} \tag{54}$$

Analysis of Eq. (54) reveals that no unlinked diagram terms occur in the sum $\mathscr{A}(T, Q, D) + \mathscr{A}(T, Q, Q_D)$, which means that Eq. (54) represents the energy contributions $2[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})]$ [see Eq. (A33) in the Appendix].

Combination of $\mathscr{A}(Q, Q, D)$ of Eq. (51) and $\mathscr{A}(Q, Q, Q_D)$ of Eq. (33) leads to

$$\mathscr{A}(Q, Q, D) + \mathscr{A}(Q, Q, Q_D) = \sum_q^{Q} \left\langle \Phi_0 \left| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V} \right| \Phi_q \right\rangle (E_0 - E_q)^{-1}$$

$$\times\left[\left\langle\Phi_q\middle|\overline{V}\hat{T}_2^{(2)}\middle|\Phi_0\right\rangle + \left\langle\Phi_q\middle|\left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_D\middle|\Phi_0\right\rangle\right]$$

$$= \left\langle\Phi_0\middle|\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2\overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}\middle|\Phi_0\right\rangle \quad (55)$$

where the connected part,

$$\left\langle\Phi_0\middle|\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2\overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}\middle|\Phi_0\right\rangle_C,$$

represents the energy contributions $E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I})$. An explicit expression for these energy terms is given in Eq. (A29) of the Appendix.

The final $E(\mathrm{MP6})_{2b}$ term can be written as

$$E(\mathrm{MP6})_{2b} = \left[E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I})\right] + 2\left[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})\right] + \left[E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I})\right]. \quad (56)$$

The three parts in Eq. (56) require $O(M^6)$, $O(M^7)$, and $O(M^6)$ computational steps. However, separate evaluation of $E_{DQD}^{(6)}$, $E_{TQD}^{(6)}$, and $E_{QQD}^{(6)}$ involves at least $O(M^8)$ operations because of the presence of the $Q$ energy denominator.

Finally, the total $E(\mathrm{MP6})_2$ contribution is obtained according to

$$E(\mathrm{MP6})_2 = E(\mathrm{MP6})_{2a_1} + E(\mathrm{MP6})_{2a_2} + E(\mathrm{MP6})_{2a_3} + E(\mathrm{MP6})_{2b}. \quad (57)$$

## DERIVATION OF $E(\mathrm{MP6})_3$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = S, D, T, Q$; $Y = T$; $X_2 = S$

The term $\mathscr{A}(X_1, T, S)$ is given by

$$\mathscr{A}(X_1, T, S) = \sum_{x_1}^{X_1}\sum_{t}^{T}(2 - \delta_{X_1,S})\left\langle\Phi_0\middle|\left(\hat{T}_2^{(1)}\right)^\dagger\overline{V}\middle|\Phi_{x_1}\right\rangle \times (E_0 - E_{x_1})^{-1}\overline{V}_{x_1 t}(E_0 - E_t)^{-1} \times\left\langle\Phi_t\middle|\overline{V}\hat{T}_1^{(2)}\middle|\Phi_0\right\rangle \quad (58)$$

with $X_1 = S, D, T, Q$. Note that contributions from $\mathscr{A}(X_1, T, X_2)$ for $X_2 = D, T, Q$ have already been covered by Eqs. (19) and (29). For the purpose of finding the linked diagram contributions of $\mathscr{A}(X_1, T, S)$, we pursue the same procedure as in the case of $E_{STQ}^{(6)}(\mathrm{II})$ and $E_{QTQ}^{(6)}(\mathrm{II})_a$ [Eqs. (43) and (44)]. Adding $\mathscr{A}(X_1, T, Q_D)$ of Eq. (33) $(Y = T)$ to Eq. (58), we obtain:

$$\mathscr{A}(X_1, T, S) + \mathscr{A}(X_1, T, Q_D) = (2 - \delta_{X_1,S})\sum_{x_1}^{X_1}\sum_{t}^{T}\left\langle\Phi_0\middle|\left(\hat{T}_2^{(1)}\right)^\dagger\overline{V}\middle|\Phi_{x_1}\right\rangle \times (E_0 - E_{x_1})^{-1}\overline{V}_{x_1 t}(E_0 - E_t)^{-1} \times\left\{\left\langle\Phi_t\middle|\overline{V}\hat{T}_1^{(2)}\middle|\Phi_0\right\rangle + \left\langle\Phi_t\middle|\left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_D\middle|\Phi_0\right\rangle\right\} \quad (X_1 = S, D, T) \quad (59)$$

and

$$\mathscr{A}(Q, T, S) + \mathscr{A}(Q, T, Q_D) = \sum_{t}^{T}\left\langle\Phi_0\middle|\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2\overline{V}\middle|\Phi_t\right\rangle(E_0 - E_t)^{-1} \times\left\{\left\langle\Phi_t\middle|\overline{V}\hat{T}_1^{(2)}\middle|\Phi_0\right\rangle + \left\langle\Phi_t\middle|\left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_D\middle|\Phi_0\right\rangle\right\}. \quad (60)$$

Using Eq. (45b), Eqs. (59) and (60) can be simplified to Eqs. (61) and (62), respectively:

$$\mathscr{A}(X_1, T, S) + \mathscr{A}(X_1, T, Q_D) = (2 - \delta_{X_1,S})\left\langle\Phi_0\middle|\left(\hat{T}_i^{(2)}\right)^\dagger\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\middle|\Phi_0\right\rangle \quad (i = 1,2,3 \text{ when } X_1 = S, D, T), \quad (61)$$

$$\mathscr{A}(Q, T, S) + \mathscr{A}(Q, T, Q_D) = \left\langle\Phi_0\middle|\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\middle|\Phi_0\right\rangle. \quad (62)$$

The last two terms in Eq. (61) $(X_1 = D, T)$ are linked diagram terms corresponding to $2[E_{DTS}^{(6)} + E_{DTQ}^{(6)}(\mathrm{I})]$ [Eq. (A25)] and $2[E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I})]$ [Eq. (A31)] while the connected parts of the first term in Eq. (61) and the term in Eq. (62), namely

$$\left\langle\Phi_0\middle|\left(\hat{T}_1^{(2)}\right)^\dagger\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\middle|\Phi_0\right\rangle_C$$

and

$$\left\langle\Phi_0\middle|\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\middle|\Phi_0\right\rangle_C$$

are identical to $E_{STS}^{(6)} + E_{STQ}^{(6)}(\mathrm{I})$ and $E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I})$ given by Eqs. (A21) and (A24) of the Appendix. Hence, the energy term $E(\mathrm{MP6})_3$ can be calculated according to

$$E(\mathrm{MP6})_3 = E_{STS}^{(6)} + E_{STQ}^{(6)}(\mathrm{I}) + 2\left[E_{DTS}^{(6)} + E_{DTQ}^{(6)}(\mathrm{I})\right] + 2\left[E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I})\right] + E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I}). \quad (63)$$

### DERIVATION OF $E(\mathrm{MP6})_4$ FROM $\mathscr{A}(X_1, Y, X_2)$ WITH $X_1 = T, Q$; $Y = P$; $X_2 = T, Q$

Finally, we consider contributions from $P$ excitations contained in $\mathscr{A}(X_1, P, X_2)$ of Eq. (18) for the case that $X_1, X_2 = T, Q$. $\mathscr{A}(X_1, P, X_2)$ covers four energy terms, of which $\mathscr{A}(T, P, Q)$ and $\mathscr{A}(Q, P, Q)$ have already been covered by Eq. (33). When replacing $\hat{T}_2^{(2)}$ $[(\hat{T}_2^{(2)})^\dagger]$ by $\hat{T}_3^{(2)}$ $[(\hat{T}_3^{(2)})]^\dagger$ or $\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2$ and $Q$ by $P$ in Eq. (52), we get

$$\begin{aligned}\mathscr{A}(T,P,T) + \mathscr{A}(T,P,Q) &= \sum_p^P \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V} \middle| \Phi_p \right\rangle (E_0 - E_p)^{-1} \\ &\quad \times \left\{ \left\langle \Phi_p \middle| \overline{V}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle + \left\langle \Phi_p \middle| \left[ \overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle \right\} \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle \end{aligned} \quad (64)$$

or

$$\begin{aligned}\mathscr{A}(Q,P,T) + \mathscr{A}(Q,P,Q) &= \sum_p^P \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V} \middle| \Phi_p \right\rangle (E_0 - E_p)^{-1} \\ &\quad \times \left\{ \left\langle \Phi_p \middle| \overline{V}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle + \left\langle \Phi_p \middle| \left[ \overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_D \middle| \Phi_0 \right\rangle \right\} \\ &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle. \end{aligned} \quad (65)$$

The connected parts of Eqs. (64) and (65) give all $P$ contributions to $E(\mathrm{MP6})$:

$$\begin{aligned} E(\mathrm{MP6})_4 &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left[ E_{TPT}^{(6)} + E_{TPQ}^{(6)} \right] + \left[ E_{QPT}^{(6)} + E_{QPQ}^{(6)} \right]. \end{aligned} \quad (66)$$

Explicit expressions for $E_{TPT}^{(6)} + E_{TPQ}^{(6)}$ and $E_{QPT}^{(6)} + E_{QPQ}^{(6)}$ are given in Eqs. (A36)–(A41) of the Appendix.

Adding all contributions $E(\mathrm{MP6})_i$ $(i = 1,2,3,4)$, the final expression for $E(\mathrm{MP6})$ is given by:

$$\begin{aligned} E(\mathrm{MP6}) &= E(\mathrm{MP6})_1 + E(\mathrm{MP6})_2 + E(\mathrm{MP6})_3 + E(\mathrm{MP6})_4 \\ &= E_{SSS}^{(6)} + 2E_{SSD}^{(6)} + 2E_{SST}^{(6)} + E_{SDS}^{(6)} \\ &\quad + 2E_{SDD}^{(6)} + 2E_{SDT}^{(6)} + E_{DSD}^{(6)} + 2E_{DST}^{(6)} \\ &\quad + E_{DDD}^{(6)} + 2E_{DDT}^{(6)} + E_{TST}^{(6)} + E_{TDT}^{(6)} \\ &\quad + E_{DTD}^{(6)} + 2E_{DTT}^{(6)} + E_{TTT}^{(6)} + E_{TQT}^{(6)} \\ &\quad + 2E_{SDQ}^{(6)} + 2E_{DDQ}^{(6)} + 2E_{TDQ}^{(6)} + E_{QDQ}^{(6)} \\ &\quad + \left[ E_{STS}^{(6)} + E_{STQ}^{(6)}(\mathrm{I}) \right] \\ &\quad + \left[ E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a \right] + E_{QTQ}^{(6)}(\mathrm{II})_b \\ &\quad + \left[ E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I}) \right] \\ &\quad + 2\left[ E_{DTS}^{(6)} + E_{DTQ}^{(6)}(\mathrm{I}) \right] + 2E_{DTQ}^{(6)}(\mathrm{II}) \\ &\quad + \left[ E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I}) \right] \\ &\quad + \left[ E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a \right] \\ &\quad + \left[ E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I}) \right] + E_{QQQ}^{(6)}(\mathrm{II})_b \\ &\quad + 2\left[ E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I}) \right] + 2E_{TTQ}^{(6)}(\mathrm{II}) \\ &\quad + 2\left[ E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I}) \right] + 2E_{TQQ}^{(6)}(\mathrm{II}) \\ &\quad + E_{QHQ}^{(6)} + \left[ E_{TPT}^{(6)} + E_{TPQ}^{(6)} \right] \\ &\quad + \left[ E_{QPT}^{(6)} + E_{QPQ}^{(6)} \right]. \end{aligned} \quad (67)$$

Expressions for all energy components given in Eq. (67) are summarized in the Appendix.

## Conclusions

The general expression for the sixth-order MP correlation energy, $E(\mathrm{MP6})$, has been dissected in the principal part $\mathscr{A}$ and renormalization terms $\mathscr{B}$, $\mathscr{C}$, and $\mathscr{D}$. Since the renormalization terms contain unlinked diagram contributions, which are canceled by corresponding terms of the principal part $\mathscr{A}$, $E(\mathrm{MP6})$ is derived solely from the linked diagram terms of the principal part $\mathscr{A}$. To identify the latter, we have investigated which of the terms $\mathscr{A}(X_1, Y, X_2)$ is associated with connected and disconnected cluster operator diagrams. Connected diagrams lead to linked diagram representations and, therefore, contributions to $E(\mathrm{MP6})$. Disconnected diagrams, upon closing, yield both linked and unlinked diagrams, which has to be considered in the derivation of $E(\mathrm{MP6})$.

We have dissected the principal part $\mathscr{A}$ into four major contributions, namely a first one with just connected cluster operator contributions, a second one with disconnected $Q$ cluster operator contributions, a third one with the corresponding $T$ contributions, and a fourth one with the corresponding $P$ contributions. Out of the latter three parts, we have extracted the linked diagram terms leading to energies $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$. Adding to these terms the linked diagram parts of the first term, collected in $E(\mathrm{MP6})_1$, an appropriate energy formula in terms of first- and second-order cluster operators has been derived for sixth-order MP perturbation theory, which can be converted into two-electron integral formulas and programmed for a computer (see Ref. [18]).

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## Appendix

In the following, we give explicit expressions for all 36 energy contributions to $E(\mathrm{MP6})$ in terms of cluster operators.

$$E^{(6)}_{SSS} = \sum_s^S \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_1^{(2)} | \Phi_0 \rangle, \quad \text{(A1)}$$

$$E^{(6)}_{SSD} = \sum_s^S \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_2^{(2)} | \Phi_0 \rangle, \quad \text{(A2)}$$

$$E^{(6)}_{SST} = \sum_s^S \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A3)}$$

$$E^{(6)}_{SDS} = \sum_d^D \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_1^{(2)} | \Phi_0 \rangle, \quad \text{(A4)}$$

$$E^{(6)}_{SDD} = \sum_d^D \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_2^{(2)} | \Phi_0 \rangle, \quad \text{(A5)}$$

$$E^{(6)}_{SDT} = \sum_d^D \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A6)}$$

$$E^{(6)}_{DSD} = \sum_s^S \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_2^{(2)} | \Phi_0 \rangle, \quad \text{(A7)}$$

$$E^{(6)}_{DST} = \sum_s^S \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A8)}$$

$$E^{(6)}_{DDD} = \sum_d^D \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_2^{(2)} | \Phi_0 \rangle, \quad \text{(A9)}$$

$$E^{(6)}_{DDT} = \sum_d^D \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A10)}$$

$$E^{(6)}_{DTD} = \sum_t^T \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_t \rangle (E_0 - E_t)^{-1} \langle \Phi_t | \bar{V} \hat{T}_2^{(2)} | \Phi_0 \rangle, \quad \text{(A11)}$$

$$E^{(6)}_{DTT} = \sum_t^T \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_t \rangle (E_0 - E_t)^{-1} \langle \Phi_t | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A12)}$$

$$E^{(6)}_{TST} = \sum_s^S \langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \bar{V} | \Phi_s \rangle (E_0 - E_s)^{-1} \langle \Phi_s | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A13)}$$

$$E^{(6)}_{TDT} = \sum_d^D \langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \langle \Phi_d | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A14)}$$

$$E^{(6)}_{TTT} = \sum_t^T \langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \bar{V} | \Phi_t \rangle (E_0 - E_t)^{-1} \langle \Phi_t | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A15)}$$

$$E^{(6)}_{TQT} = \sum_q^Q \langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \bar{V} | \Phi_q \rangle (E_0 - E_q)^{-1} \langle \Phi_q | \bar{V} \hat{T}_3^{(2)} | \Phi_0 \rangle, \quad \text{(A16)}$$

$$E^{(6)}_{SDQ} = \sum_d^D \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \times \left\langle \Phi_d \middle| \left[ \bar{V} \tfrac{1}{2} (\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A17)}$$

$$E^{(6)}_{DDQ} = \sum_d^D \langle \Phi_0 | (\hat{T}_2^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \times \left\langle \Phi_d \middle| \left[ \bar{V} \tfrac{1}{2} (\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A18)}$$

$$E^{(6)}_{TDQ} = \sum_d^D \langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \bar{V} | \Phi_d \rangle (E_0 - E_d)^{-1} \times \left\langle \Phi_d \middle| \left[ \bar{V} \tfrac{1}{2} (\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A19)}$$

$$E^{(6)}_{QDQ} = \sum_d^D \left\langle \Phi_0 \middle| \left[ \tfrac{1}{2} \left( (\hat{T}_2^{(1)})^\dagger \right)^2 \bar{V} \right]_C \middle| \Phi_d \right\rangle (E_0 - E_d)^{-1} \times \left\langle \Phi_d \middle| \left[ \bar{V} \tfrac{1}{2} (\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A20)}$$

$$E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I}) = \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger \bar{V} \hat{T}_2^{(1)} \hat{T}_1^{(2)} | \Phi_0 \rangle_C = \langle \Phi_0 | (\hat{T}_1^{(2)})^\dagger (\bar{V} \hat{T}_2^{(1)} \hat{T}_1^{(2)})_C | \Phi_0 \rangle, \quad \text{(A21)}$$

$$E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a = \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_1^{(2)})^\dagger \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A22)}$$

$$E_{QTQ}^{(6)}(\mathrm{II})_b = \sum_t^T \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \overline{V} \right\}_C \middle| \Phi_t \right\rangle \times (E_0 - E_t)^{-1} \left\langle \Phi_t \middle| \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A23)}$$

$$\begin{aligned} E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_1^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 (\overline{V}\hat{T}_2^{(1)}\hat{T}_1^{(2)})_D \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \hat{T}_2^{(1)}(\overline{V}\hat{T}_1^{(2)})_C \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \hat{T}_1^{(2)}(\overline{V}\hat{T}_2^{(1)})_C \middle| \Phi_0 \right\rangle_C, \end{aligned} \quad \text{(A24)}$$

$$E_{DTS}^{(6)} + E_{DTQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| (\hat{T}_2^{(2)})^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_1^{(2)} \middle| \Phi_0 \right\rangle_C, \quad \text{(A25)}$$

$$E_{DTQ}^{(6)}(\mathrm{II}) = \sum_t^T \left\langle \Phi_0 \middle| (\hat{T}_2^{(2)})^\dagger \overline{V} \middle| \Phi_t \right\rangle (E_0 - E_t)^{-1} \times \left\langle \Phi_t \middle| \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A26)}$$

$$E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| (\hat{T}_2^{(2)})^\dagger (\overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)})_C \middle| \Phi_0 \right\rangle, \quad \text{(A27)}$$

$$E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a = \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A28)}$$

$$\begin{aligned} E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_D \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle \\ &= \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \hat{T}_2^{(1)}(\overline{V}\hat{T}_2^{(1)})_C \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| (\hat{T}_2^{(1)})^\dagger (\hat{T}_2^{(2)})^\dagger \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \end{aligned} \quad \text{(A29)}$$

$$E_{QQQ}^{(6)}(\mathrm{II})_b = \sum_q^Q \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \overline{V} \right\}_C \middle| \Phi_q \right\rangle (E_0 - E_q)^{-1} \times \left\langle \Phi_q \middle| \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A30)}$$

$$E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle_C, \quad \text{(A31)}$$

$$E_{TTQ}^{(6)}(\mathrm{II}) = \sum_t^T \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \overline{V} \middle| \Phi_t \right\rangle (E_0 - E_t)^{-1} \times \left\langle \Phi_t \middle| \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A32)}$$

$$E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \overline{V}\hat{T}_2^{(2)}\hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle_C, \quad \text{(A33)}$$

$$E_{TQQ}^{(6)}(\mathrm{II}) = \sum_q^Q \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \overline{V} \middle| \Phi_q \right\rangle (E_0 - E_q)^{-1} \times \left\langle \Phi_q \middle| \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle, \quad \text{(A34)}$$

$$\begin{aligned} E_{QHQ}^{(6)} &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \hat{T}_2^{(1)} \left[ \overline{V}\tfrac{1}{2}(\hat{T}_2^{(1)})^2 \right]_C \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \left[ \overline{V}\frac{1}{3!}(\hat{T}_2^{(1)})^3 \right]_C \middle| \Phi_0 \right\rangle, \end{aligned} \quad \text{(A35)}$$

$$\begin{aligned} E_{TPT}^{(6)} + E_{TPQ}^{(6)} &= \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_D \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle \\ &= [E_{TPT}^{(6)}(\mathrm{I}) + E_{TPQ}^{(6)}(\mathrm{I})] + [E_{TPT}^{(6)}(\mathrm{II}) + E_{TPQ}^{(6)}(\mathrm{II})], \end{aligned} \quad \text{(A36)}$$

where

$$\begin{aligned} E_{TPT}^{(6)}(\mathrm{I}) + E_{TPQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_D \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger \hat{T}_2^{(1)} (\overline{V}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle_C \end{aligned} \quad \text{(A37)}$$

and

$$E_{TPT}^{(6)}(\mathrm{II}) + E_{TPQ}^{(6)}(\mathrm{II}) = \left\langle \Phi_0 \middle| (\hat{T}_3^{(2)})^\dagger (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle \quad \text{(A38)}$$

$$\begin{aligned} E_{QPT}^{(6)} + E_{QPQ}^{(6)} &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_D \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle \\ &= [E_{QPT}^{(6)}(\mathrm{I}) + E_{QPQ}^{(6)}(\mathrm{I})] + [E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})] \end{aligned} \quad \text{(A39)}$$

where

$$\begin{aligned} E_{QPT}^{(6)}(\mathrm{I}) + E_{QPQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_D \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \hat{T}_2^{(1)}(\overline{V}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 \hat{T}_3^{(2)}(\overline{V}\hat{T}_2^{(1)})_C \middle| \Phi_0 \right\rangle_C \end{aligned} \quad \text{(A40)}$$

and

$$E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II}) = \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[(\hat{T}_2^{(1)})^\dagger\right]^2 (\overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)})_C \middle| \Phi_0 \right\rangle \quad \text{(A41)}$$

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