Sixth-Order Many-Body Perturbation Theory. II. Implementation and Application

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ABSTRACT

Based on a cluster operator formulation of sixth-order Møller–Plesset (MP6) perturbation theory equations for the calculation of MP6 in terms of spin-orbital two-electron integrals are derived. Efficiency has been gained by systematically using intermediate arrays for the determination of energy contributions resulting from disconnected cluster operators. In this way, the maximum cost factor of $O(M^{12})$ (M being number of basis functions) is reduced to $O(M^9)$. The implementation of MP6 on a computer is described. The reliability of calculated MP6 correlation energies has been checked in three different ways, namely (a) by comparison with full configuration interaction (CI) results, (b) by using alternative computational routines that do not involve intermediate arrays, and (c) by taking advantage of relationships between fifth-order and sixth-order energy contributions. First applications of the MP6 method are presented.

Introduction

This is the second article in a series of four studies [1–3], which will describe the development and application of sixth-order many-body perturbation theory (MBPT) in connection with the Møller–Plesset (MP) perturbation operator [4] for the purpose of getting improved correlation energies for atoms and molecules in a routine way. At sixth-order MP–MBPT (MP6), correlation effects are described by single (S), double (D), triple (T), quadruple (Q), pentuple (P), and hextuple (H) excitations, where the P and H excitations lead to new correlation effects not covered by any of the perturbation methods of lower order. In addition, MP6 provides a refined description of the coupling between different excitations, which helps to further reduce an overestimation of correlation effects at lower orders. Of course, coupling between P or H excitations is not included at MP6 and, there-

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fore, the correlation effects associated with P and H excitations will be somewhat exaggerated at the sixth-order level.

In the first article in the series [1], we have derived explicit expressions for the 36 energy contributions to the sixth-order energy E(MP6) using a cluster operator notation. In this study, we will transform the 36 energy terms into appropriate spin-orbital two-electron integral formulas, which can directly be calculated with a computer provided appropriate computer programs are developed. Because of this, we will also describe the implementation of such programs on a vector computer and discuss first application of the MP6 method to atoms and molecules. Then, in the third article [2], we will present various size-extensive MP6 methods, which can be used to analyze different energy contributions to E(MP6) or to apply MP6 to larger than the small test molecules we will discuss in this study.

Although the development of the E(MP6) expression in the first series [1] has been done in an algebraic way, the derivation of each part of E(MP6) was based on the characteristics of its diagrammatic representation. All terms of the general E(MP6) expression can be associated with connected and disconnected cluster operator diagrams. This dissection facilitates the identification of linked and unlinked diagram terms. We have distinguished between four major contributions to E(MP6), namely $E(\mathrm{MP6})_1$, $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$. The first part, $E(\mathrm{MP6})_1$, covers just contributions resulting from connected cluster operator diagrams, which lead to linked diagram terms and, according to the linked diagram theorem [5], fully contribute to the E(MP6) energy. The other parts cover contributions from the T, Q, or P disconnected cluster operators $\hat{T}_1\hat{T}_2$, $\frac{1}{2}\hat{T}_2^2$, or $\hat{T}_2\hat{T}_3$. $E(\mathrm{MP6})_2$ covers those Q contributions which lead to linked diagram terms. Similarly, $E(\mathrm{MP6})_3$ covers the linked diagram terms resulting from T contributions while $E(\mathrm{MP6})_4$ contains the corresponding P contributions.

In this study, we will stepwise transform the cluster operator expressions of the first study into two-electron integral formulas. This will be straightforward in the case of those terms resulting from connected cluster operator diagrams. However, for the disconnected cluster operator diagram contributions involving higher excitations (e.g., $E^{(6)}_{QHQ}$, $E^{(6)}_{QPQ}$) transformation will result into two-electron integral formulas, which are very costly to calculate on a computer. In these cases, the introduction of intermediate arrays that reduce computational cost will be essential. In the case of MP6, there are several possibilities to define intermediate arrays and to reduce the computational cost to a minimum. We will present here one way which we have found to be suitable for setting up a MP6 computer program.

In the following section, an E(MP6) energy expression will be derived in terms of two-electron integrals that can be programmed for a computer. For this purpose, we will first consider all connected cluster operator terms of $E(\mathrm{MP6})_1$. Then, we will discuss disconnected Q cluster operator terms contained in $E(\mathrm{MP6})_2$, followed by the disconnected T cluster operator contributions of $E(\mathrm{MP6})_3$ and the disconnected P cluster operator contributions of $E(\mathrm{MP6})_4$. In this way, we follow the procedure applied in the first article of the series for the derivation of the energy formula in terms of cluster operators. In the third section, we will describe the implementation of an appropriate program for the calculation of the sixth-order correlation energy E(MP6) on a vector computer. In this connection, we will particularly focus on the testing of the reliability of calculated E(MP6) values because this is a major problem in programs of this size and degree of complication. Finally, some applications of the new MP6 method will be discussed.

Derivation of the Sixth-Order Energy E(MP6) in Terms of Two-Electron Integral Formulas

We first consider the energy terms $E^{(6)}_{X_1YX_2}$ associated with connected cluster operator diagrams (see Eqs. (28) and (29) of [1]),

$$E^{(6)}_{X_1YX_2} = \sum_{i,j}^{1,2,3} \sum_{y}^{Y} \left\langle \Phi_0 \middle| \left(\hat{T}_i^{(2)}\right)^{\dagger} \overline{V} \middle| \Phi_y \right\rangle \times (E_0 - E_y)^{-1} \left\langle \Phi_y \middle| \overline{V} \hat{T}_j^{(2)} \middle| \Phi_0 \right\rangle \quad (i \text{ or } j = 1,2,3 \text{ for } X_1 \text{ or } X_2 = S, D, T), \tag{1}$$

where excitations $Y = S, D, T, Q$ are denoted by subscript $y = s, d, t, q$. For P, H or general excita-

tions X, we will use subscripts p, h, and x, respectively. In Eq. (1), energies E_0 and E_y are eigenvalues of the unperturbed Hamiltonian $\hat{H}_0$ corresponding to the Hartree–Fock (HF) reference function $|\Phi_0\rangle$ and the y-fold excited eigenfunction $|\Phi_y\rangle$. The MP perturbation operator $\overline{V}$ and total Hamiltonian are defined by

$$\overline{V} = \hat{V} - \langle\Phi_0|\hat{V}|\Phi_0\rangle \tag{2}$$

and

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{3}$$

The cluster operators $\hat{T}_i^{(2)}$ $(i = 1,2,3)$ at second-order perturbation theory are given by

$$\hat{T}_i^{(2)}|\Phi_0\rangle = \sum_x^X b_x|\Phi_x\rangle \qquad (X = S, D, T \text{ for } i = 1,2,3) \tag{4}$$

where the amplitudes $b_x (x = s, d, t)$ are defined by

$$b_x = (E_0 - E_x)^{-1}\langle\Phi_x|\overline{V}\hat{T}_2^{(1)}|\Phi_0\rangle, \tag{5}$$

with the double excitation cluster $\hat{T}_2^{(1)}$ at first-order being

$$\hat{T}_2^{(1)}|\Phi_0\rangle = \sum_d^D a_d|\Phi_d\rangle \tag{6}$$

and the first-order amplitude a_d being

$$a_d = (E_0 - E_d)^{-1}\langle\Phi_d|\hat{V}|\Phi_0\rangle. \tag{7}$$

Both first-order and second-order amplitudes can easily be expressed in terms of two-electron integrals as is shown in Eqs. (A1)–(A4) of the Appendix.

DERIVATION OF TWO-ELECTRON INTEGRAL FORMULAS FOR $E(\mathrm{MP6})_1$

The sum of all energy terms $E^{(6)}_{X_1YX_2}$ defined in Eq. (1) is equal to $E(\mathrm{MP6})_1$ [1] and can be expressed by Eq. (8):

$$E(\mathrm{MP6})_1 = \left[\sum_{X_1,X_2}^{S,D,T}\sum_{Y}^{S,D} + \sum_{X_1,X_2}^{D,T}\sum_{Y}^{T} + \sum_{X_1,X_2}^{T}\sum_{Y}^{Q}\right] \times E^{(6)}_{X_1YX_2}. \tag{8}$$

$E(\mathrm{MP6})_1$ covers 16 different energy terms resulting from S, D, and T excitations. When converting the matrix elements $\langle\Phi_y|\overline{V}\hat{T}_i^{(2)}|\Phi_0\rangle$ $(y = s, d, t, q;$ $i = 1,2,3)$ in Eq. (1) into a two-electron integral form, one obtains the arrays u_1–u_9 listed in Table I. With the help of arrays u_1–u_9, one can derive two-electron integral formulas for the 16 energy terms of $E(\mathrm{MP6})_1$ in a relatively simple form. For example,

$$E^{(6)}_{SSS} = \sum_{ia}\frac{u_1(i,a)u_1(i,a)}{\epsilon_i - \epsilon_a}, \tag{9}$$

$$E^{(6)}_{SDS} = \frac{1}{4}\sum_{ij}\sum_{ab}\frac{u_4(ij,ab)u_4(ij,ab)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \tag{10}$$

$$E^{(6)}_{DTT} = \frac{1}{(3!)^2}\sum_{ijk}\sum_{abc}\frac{u_7(ijk,abc)u_8(ijk,abc)}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \tag{11}$$

$$E^{(6)}_{TTT} = \frac{1}{(3!)^2}\sum_{ijk}\sum_{abc}\frac{u_8(ijk,abc)u_8(ijk,abc)}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \tag{12}$$

$$E^{(6)}_{TQT} = \frac{1}{(4!)^2}\sum_{ijkl}\sum_{abcd} \times \frac{u_9(ijkl,abcd)u_9(ijkl,abcd)}{\epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b - \epsilon_c - \epsilon_d}. \tag{13}$$

In Eqs. (9)–(13), indices $i, j, k, l, \ldots$ denote occupied spin orbitals while $a, b, c, d, \ldots$ represent virtual spin orbitals. According to Table I, calculation of arrays $u_6(ij,ab)$ [or $u_7(ijk,abc)$], $u_8(ijk,abc)$, and $u_9(ijkl,abcd)$ requires $O(M^7)$, $O(M^8)$, and $O(M^9)$ computational steps while calculation of the other arrays involves just $O(M^6)$ or even less steps (M being number of basis functions).

Two-electron integral expressions for all 16 terms of $E(\mathrm{MP6})_1$ can be constructed with the help of Tables I and II. Comparing the various $E(\mathrm{MP6})_1$ terms in Table II, it becomes obvious that evaluation of $E^{(6)}_{TQT}$ is most costly because it requires calculation of array $u_9(ijkl,abcd)$.

DERIVATION OF TWO-ELECTRON INTEGRAL FORMULAS FOR $E(\mathrm{MP6})_2$

The energy part $E(\mathrm{MP6})_2 = E(\mathrm{MP6})_{2a} + E(\mathrm{MP6})_{2b}$ contains contributions associated with the disconnected Q cluster operator [1]. $E(\mathrm{MP6})_{2a}$

TABLE I
Definition of arrays u_1–u_9.[a]

Arrays	Expressions	Two-electron integral formulas	Cost
$u_1(i,a)$	$\langle\Phi_i^a\|\bar{V}\hat{T}_1^{(2)}\|\Phi_0\rangle$	$-\Sigma_{me}\langle ma\|\|ie\rangle b_m^e$	$O(M^5)$
$u_2(i,a)$	$\langle\Phi_i^a\|\bar{V}\hat{T}_2^{(2)}\|\Phi_0\rangle$	$-\frac{1}{2}[\Sigma_{mef}\langle ma\|\|ef\rangle b_{im}^{ef}+\Sigma_{mne}\langle mn\|\|ie\rangle b_{mn}^{ae}]$	$O(M^6)$
$u_3(i,a)$	$\langle\Phi_i^a\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\frac{1}{4}\Sigma_{mnef}\langle mn\|\|ef\rangle b_{imn}^{aef}$	$O(M^7)$
$u_4(ij,ab)$	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_1^{(2)}\|\Phi_0\rangle$	$\Sigma_e\Sigma_P(-1)^P P(i/j)\langle ab\|\|ej\rangle b_i^e$ $+\Sigma_m\Sigma_P(-1)^P P(a/b)\langle ma\|\|ij\rangle b_m^b$	$O(M^5)$
$u_5(ij,ab)$	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_2^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}[\Sigma_{ef}\langle ab\|\|ef\rangle b_{ij}^{ef}+\Sigma_{mn}\langle mn\|\|ij\rangle b_{mn}^{ab}]$ $-\Sigma_{me}\Sigma_P(-1)^P P(i/j\|a/b)\langle mb\|\|je\rangle b_{im}^{ae}$	$O(M^6)$
$u_6(ij,ab)$	$\langle\Phi_{ij}^{ab}\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}[\Sigma_{mef}\Sigma_P(-1)^P P(a/b)\langle bm\|\|ef\rangle b_{ijm}^{aef}$ $+\Sigma_{mne}\Sigma_P(-1)^P P(i/j)\langle mn\|\|ej\rangle b_{imn}^{abe}]$	$O(M^7)$
$u_7(ijk,abc)$	$\langle\Phi_{ijk}^{abc}\|\bar{V}\hat{T}_2^{(2)}\|\Phi_0\rangle$	$\Sigma_P(-1)^P P(i/ij\|a/bc)[\Sigma_e\langle bc\|\|ei\rangle b_{jk}^{ae}-\Sigma_m\langle ma\|\|jk\rangle b_{im}^{bc}]$	$O(M^7)$
$u_8(ijk,abc)$	$\langle\Phi_{ijk}^{abc}\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\frac{1}{2}[\Sigma_{ef}\Sigma_P(-1)^P P(a/bc)\langle bc\|\|ef\rangle b_{ijk}^{aef}$ $+\Sigma_{mn}\Sigma_P(-1)^P P(i/jk)\langle mn\|\|jk\rangle b_{imn}^{abc}]$ $-\Sigma_{me}\Sigma_P(-1)^P P(i/jk\|a/bc)\langle ma\|\|ie\rangle b_{jkm}^{bce}$	$O(M^8)$
$u_9(ijkl,abcd)$	$\langle\Phi_{ijkl}^{abcd}\|\bar{V}\hat{T}_3^{(2)}\|\Phi_0\rangle$	$\Sigma_e\Sigma_P(-1)^P P(i/jkl\|ab/cd)\langle ie\|\|ab\rangle b_{jkl}^{cde}$ $+\Sigma_m\Sigma_P(-1)^P P(ij/jk\|a/bcd)\langle ij\|\|ma\rangle b_{mkl}^{bcd}$	$O(M^9)$

[a] $(-1)^P\Sigma_P P(i/j)$ [$P(i/jk)$] denotes the sum of the identity and the permutation(s) of i with j (and k) while the permutation symbol $P(i/j|a/b)$ [or $P(i/jk|a/ab)$] stands for $P(i/j)P(a/b)$ [or $P(i/jk)P(a/bc)$]. Note that in a symbol such as $P(i/jkl|ab/cd)$ [$=P(i/jkl)P(ab/cd)$] permutations $a\leftrightarrow b$ and $c\leftrightarrow d$ are excluded.

covers all energy terms involving the disconnected operator $\frac{1}{2}(\hat{T}_2^{(1)})^2$. These are the contributions $\langle\Phi_y|[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_C|\Phi_0\rangle$ with (1) $y=d$ and (2) $y=t$, q, and (3) $y=h$, namely $\langle\Phi_q|[\bar{V}(1/3!)(\hat{T}_2^{(1)})^3]_C|\Phi_0\rangle$ and $\langle\Phi_q|\hat{T}_2^{(1)}[\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_C|\Phi_0\rangle$, which correspond to the connected part of $\langle\Phi_q|\bar{V}|\Phi_h\rangle(E_0-E_h)^{-1}\langle\Phi_h|\bar{V}\frac{1}{2}(\hat{T}_2^{(1)})^2|\Phi_0\rangle$. Hence, $E(\mathrm{MP6})_{2a}$ can be expressed by the following equations:

$$E(\mathrm{MP6})_{2a} = E(\mathrm{MP6})_{2a_1} + E(\mathrm{MP6})_{2a_2} + E(\mathrm{MP6})_{2a_3}, \tag{14}$$

where

$$E(\mathrm{MP6})_{2a_1} = 2\sum_{i}^{1,2,3}\sum_{d}^{D}\left\langle\Phi_0\middle|\left(\hat{T}_i^{(2)}\right)^\dagger\bar{V}\middle|\Phi_d\right\rangle \times(E_0-E_d)^{-1}\left\langle\Phi_d\middle|\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle + \sum_{d}^{D}\left\langle\Phi_0\middle|\left[\tfrac{1}{2}\left(\left(\hat{T}_2^{(1)}\right)^\dagger\right)^2\bar{V}\right]_C\middle|\Phi_d\right\rangle \times(E_0-E_d)^{-1}\left\langle\Phi_d\middle|\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \tag{15}$$

$$= 2E_{SDQ}^{(6)} + 2E_{DDQ}^{(6)} + 2E_{TDQ}^{(6)} + E_{QDQ}^{(6)} \tag{16}$$

$$\begin{aligned}E(\mathrm{MP6})_{2a_2} &= \left\langle\Phi_0\middle|\left(\hat{T}_1^{(2)}\right)^\dagger\left(\hat{T}_2^{(1)}\right)^\dagger\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \\ &+ \left\langle\Phi_0\middle|\left(\hat{T}_2^{(2)}\right)^\dagger\left(\hat{T}_2^{(1)}\right)^\dagger\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \\ &+ \sum_{y}^{T,Q}\left\langle\Phi_0\middle|\left[\tfrac{1}{2}\left[\left(\left(\hat{T}_2^{(1)}\right)^\dagger\right)^2\bar{V}\right]_C\middle|\Phi_y\right\rangle(E_0-E_y)^{-1}\left\langle\Phi_y\middle|\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \\ &+ 2\sum_{i}^{2,3}\sum_{t}^{T}\left\langle\Phi_0\middle|\left(\hat{T}_i^{(2)}\right)^\dagger\bar{V}\middle|\Phi_t\right\rangle(E_0-E_t)^{-1}\left\langle\Phi_t\middle|\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \\ &+ 2\sum_{q}^{Q}\left\langle\Phi_0\middle|\left(\hat{T}_3^{(2)}\right)^\dagger\bar{V}\middle|\Phi_q\right\rangle(E_0-E_q)^{-1}\left\langle\Phi_q\middle|\left[\bar{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C\middle|\Phi_0\right\rangle \end{aligned} \tag{17}$$

$$\begin{aligned}&= \left[E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a\right] + \left[E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a\right] \\ &+ E_{QTQ}^{(6)}(\mathrm{II})_b + E_{QQQ}^{(6)}(\mathrm{II})_b + 2E_{DTQ}^{(6)}(\mathrm{II}) + 2E_{TTQ}^{(6)}(\mathrm{II}) + 2E_{TQQ}^{(6)}(\mathrm{II})\end{aligned} \tag{18}$$

TABLE II
Definition of the 16 energy terms of $E(\mathrm{MP6})_1$ [Eq. (8)] as products of arrays u_i and u_j ($i, j = 1, \ldots, 9$).[a]

Arrays u_i, u_j	$u_1(i,a)$	$u_2(i,a)$	$u_3(i,a)$	$u_4(ij,ab)$	$u_5(ij,ab)$	$u_6(ij,ab)$	$u_7(ijk,abc)$	$u_8(ijk,abc)$	$u_9(ijkl,abcd)$
$\frac{u_1(i,a)}{\Delta_i^a}$	$E_{SSS}^{(6)}$	$E_{SSD}^{(6)}$	$E_{SST}^{(6)}$						
$\frac{u_2(i,a)}{\Delta_i^a}$		$E_{DSD}^{(6)}$	$E_{DST}^{(6)}$						
$\frac{u_3(i,a)}{\Delta_i^a}$			$E_{TST}^{(6)}$						
$\frac{u_4(ij,ab)}{\Delta_{ij}^{ab}}$				$E_{SDS}^{(6)}$	$E_{SDD}^{(6)}$	$E_{SDT}^{(6)}$			
$\frac{u_5(ij,ab)}{\Delta_{ij}^{ab}}$					$E_{DDD}^{(6)}$	$E_{DDT}^{(6)}$			
$\frac{u_6(ij,ab)}{\Delta_{ij}^{ab}}$						$E_{TDT}^{(6)}$			
$\frac{u_7(ijk,abc)}{\Delta_{ijk}^{abc}}$							$E_{DTD}^{(6)}$	$E_{DTT}^{(6)}$	
$\frac{u_8(ijk,abc)}{\Delta_{ijk}^{abc}}$								$E_{TTT}^{(6)}$	
$\frac{u_9(ijkl,abcd)}{\Delta_{ijkl}^{abcd}}$									$E_{TQT}^{(6)}$

[a] Δ_i^a, Δ_{ij}^{ab}, Δ_{ijk}^{abc}, and Δ_{ijkl}^{abcd} are given by

$$\Delta_i^a = \epsilon_i - \epsilon_a$$

$$\Delta_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

$$\Delta_{ijk}^{abc} = \epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$$

$$\Delta_{ijkl}^{abcd} = \epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b - \epsilon_c - \epsilon_d$$

$$E(\mathrm{MP6})_{2a_3} = \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \hat{T}_2^{(1)}\left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C \middle| \Phi_0 \right\rangle_C + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left[\overline{V}\frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3\right]_C \middle| \Phi_0 \right\rangle \quad (19)$$

$$= E_{QHQ}^{(6)}(\mathrm{I}) + E_{QHQ}^{(6)}(\mathrm{II}). \quad (20)$$

In Eq. (15), all energy terms contain the same matrix element $\langle \Phi_d | [\overline{V}\frac{1}{2}(\hat{T}_2^{(1)})^2]_C | \Phi_0 \rangle$, for which a two-electron integral form is given by Eqs. (21) and (22), respectively.

$$u_{10}(ij,ab) = \left\langle \Phi_{ij}^{ab} \middle| \left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2\right]_C \middle| \Phi_0 \right\rangle = \frac{1}{4}\sum_{mn}\sum_{ef}\langle mn||ef\rangle \times \left[a_{ij}^{ef}a_{mn}^{ab} - 2\sum_P (-1)^P P(a/b) a_{ij}^{ae}a_{mn}^{bf} - 2\sum_P (-1)^P P(i/j) a_{im}^{ab}a_{jn}^{ef} + 4\sum_P (-1)^P P(i/j) a_{im}^{ae}a_{jn}^{bf} \right] \quad (21)$$

$$= \frac{1}{2}\sum_{mn} z_1(ij,mn) a_{mn}^{ab} - \sum_e \sum_P (-1)^P P(a/b) z_2(b,e) a_{ij}^{ae} + \sum_m \sum_P (-1)^P (i/j) z_3(j,m) a_{im}^{ab} + \sum_{nf} \sum_P (-1)^P (i/j) z_4(ia,nf) a_{jn}^{bf}. \quad (22)$$

Here, the permutation symbol $P(i/j)$ [or $P(a/b)$]

TABLE III
Definition of intermediate arrays z_1–z_{19}.

Intermediate array	Expression	Cost
$z_1(ij, mn)$	$\frac{1}{2}\Sigma_{ef}\langle mn\|\|ef\rangle a_{ij}^{ef}$	$O(M^6)$
$z_2(b, e)$	$\frac{1}{2}\Sigma_{mn,f}\langle mn\|\|ef\rangle a_{mn}^{bf}$	$O(M^5)$
$z_3(j, m)$	$-\frac{1}{2}\Sigma_{n,ef}\langle mn\|\|ef\rangle a_{jn}^{ef}$	$O(M^5)$
$z_4(ia, nf)$	$\Sigma_{m,e}\langle mn\|\|ef\rangle a_{im}^{ae}$	$O(M^6)$
$z_5(i, bc, f)$	$\Sigma_{me}\Sigma_P(-1)^P P(b/c)\langle mb\|\|ef\rangle a_{im}^{ce} - \frac{1}{2}\Sigma_{mn}\langle mn\|\|if\rangle a_{mn}^{bc}$	$O(M^6)$
$z_6(jk, m, a)$	$\frac{1}{2}\Sigma_{ef}\langle am\|\|ef\rangle a_{jk}^{ef} + \Sigma_{ne}\Sigma_P(-1)^P P(j/k)\langle mn\|\|ej\rangle a_{kn}^{ae}$	$O(M^6)$
$z_7(cd, jkl, m)$	$\Sigma_P(-1)^P P(j/kl)[\frac{1}{2}\Sigma_n\langle kl\|\|mn\rangle a_{jn}^{cd} - \Sigma_e\Sigma_{P'}(-1)^{P'}P'(c/d)\langle mc\|\|je\rangle a_{kl}^{de}]$	$O(M^7)$
$z_8(bcd, kl, e)$	$\frac{1}{2}\Sigma_f\Sigma_P(-1)^P P(b/cd)\langle cd\|\|ef\rangle a_{kl}^{bf}$	$O(M^7)$
$z_9(i, bc, f)$	$-\Sigma_e\langle bc\|\|ef\rangle b_i^e - \Sigma_m(\langle mb\|\|if\rangle b_m^c - \langle mc\|\|if\rangle b_m^b)$	$O(M^5)$
$z_{10}(jk, l, a)$	$-\Sigma_m\langle jk\|\|ml\rangle b_m^a - \Sigma_e(\langle la\|\|je\rangle b_k^e - \langle la\|\|ke\rangle b_j^e)$	$O(M^5)$
$z_{11}(mn, jk)$	$\frac{1}{2}\Sigma_{ef}\langle mn\|\|ef\rangle a_{jk}^{ef}$	$O(M^6)$
$z_{12}(i, m)$	$-\frac{1}{2}\Sigma_{n,ef}\langle mn\|\|ef\rangle a_{in}^{ef}$	$O(M^5)$
$z_{13}(bc, ef)$	$\frac{1}{2}\Sigma_{mn}\langle mn\|\|ef\rangle a_{mn}^{bc}$	$O(M^6)$
$z_{14}(a, e)$	$-\frac{1}{2}\Sigma_{mn,f}\langle mn\|\|ef\rangle a_{mn}^{af}$	$O(M^5)$
$z_{15}(ma, ie)$	$\Sigma_{n,f}\langle mn\|\|ef\rangle a_{in}^{af}$	$O(M^6)$
$z_{16}(i, bc, f)$	$-\frac{1}{2}\Sigma_{mn,e}\langle mn\|\|ef\rangle b_{imn}^{ebc}$	$O(M^7)$
$z_{17}(jk, n, a)$	$-\frac{1}{2}\Sigma_{m,ef}\langle mn\|\|ef\rangle b_{mjk}^{aef}$	$O(M^7)$
$z_{18}(j, a, bc)$	$\frac{1}{2}\Sigma_{kl,d}a_{kl}^{ad}b_{jkl}^{bcd}$	$O(M^7)$

denotes the sum of the identity and the permutation of $i(a)$ and $j(b)$. The arrays $z_1(ij, mn)$, $z_2(b, e)$, $z_3(j, m)$, and $z_4(ia, nf)$, which appear in expression (22), are defined in Table III. They represent intermediate arrays introduced to reduce the calculation of $u_{10}(ij, ab)$ from $O(M^8)$ to $O(M^6)$ steps.

With the help of arrays $u_4(ij, ab)$, $u_5(ij, ab)$, $u_6(ij, ab)$, and $u_{10}(ij, ab)$ (see Table I), one can derive two-electron integral formulas for each energy term of $E(\mathrm{MP6})_{2a_1}$ in Eq. (16). For example, $E_{SDQ}^{(6)}$ is given by Eq. (23):

$$\begin{aligned} E_{SDQ}^{(6)} &= \left\langle \Phi_0 \middle| \left(\hat{T}_1^{(2)}\right)^\dagger \overline{V} \middle| \Phi_d \right\rangle (E_0 - E_d)^{-1} \\ &\quad \times \left\langle \Phi_d \middle| \left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle \\ &= \frac{1}{4}\sum_{ij}\sum_{ab} \frac{u_4(ij, ab)u_{10}(ij, ab)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \end{aligned} \quad (23)$$

Similar expressions are obtained for $E_{DDQ}^{(6)}$, $E_{TDQ}^{(6)}$, and $E_{QDQ}^{(6)}$ by replacing $u_4(ij, ab)$ in Eq. (23) by arrays $u_5(ij, ab)$, $u_6(ij, ab)$, and $u_{10}(ij, ab)$.

The determination of $E(\mathrm{MP6})_{2a_2}$ involves the calculation of matrix elements

$$\left\langle \Phi_t \middle| \left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle \text{ and } \left\langle \Phi_q \middle| \left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle.$$

The latter are given by u_{11} and u_{12}, respectively, in Eqs. (24), (25), and (26):

$$\begin{aligned} u_{11}(ijk, abc) &= \left\langle \Phi_{ijk}^{abc} \middle| \left[\overline{V}\tfrac{1}{2}\left(\hat{T}_2^{(1)}\right)^2 \right]_C \middle| \Phi_0 \right\rangle \\ &= \sum_P (-1)^P P(i/jk|a/bc) \\ &\quad \times \Bigg\{ \sum_{mef} \Big[(\langle mb\|ef\rangle a_{im}^{ce} - \langle mc\|ef\rangle a_{im}^{be}) a_{jk}^{af} \\ &\quad + \tfrac{1}{2}\langle am\|ef\rangle a_{jk}^{ef} a_{im}^{bc} \Big] \\ &\quad - \sum_{mne} \Big[(\langle mn\|ej\rangle a_{km}^{ae} - \langle mn\|ek\rangle a_{jm}^{ae}) a_{in}^{bc} \\ &\quad + \tfrac{1}{2}\langle mn\|ie\rangle a_{mn}^{bc} a_{jk}^{ae} \Big] \Bigg\} \end{aligned} \quad (24)$$

$$\begin{aligned} &= \sum_P (-1)^P P(i/jk|a/bc) \\ &\quad \times \left[\sum_f z_5(i, bc, f) a_{jk}^{af} + \sum_m z_6(jk, m, a) a_{im}^{bc} \right]. \end{aligned} \quad (25)$$

$$u_{12}(ijkl, abcd) = \left\langle \Phi_{ijkl}^{abcd} \middle| \left[\bar{V}_2^1 \left(\hat{T}_2^{(1)} \right)^2 \right]_C \middle| \Phi_0 \right\rangle$$
$$= -\sum_m \sum_P (-1)^P P(i/jkl|ab/cd) \times z_7(cd, jkl, m) a_{im}^{ab} - \sum_e \sum_P (-1)^P P(ij/kl|a/bcd) \times z_8(bcd, kl, e) a_{ij}^{ae}, \quad (26)$$

where the intermediate arrays $z_5(i, bc, f)$, $z_6(jk, ma)$, $z_7(cd, jkl, m)$, and $z_8(bcd, kl, e)$ are given in Table III. Utilizing arrays $u_{11}(ijk, abc)$ and $u_{12}(ijkl, abcd)$ [Eqs. (25) and (26)], expressions (27)–(33) can be derived for the seven energy terms of $E(\mathrm{MP6})_{2a_2}$ shown in Eq. (18):

$$E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a = \sum_{ia} b_i^a \left[\frac{1}{4} \sum_{jk, bc} a_{jk}^{bc} u_{11}(ijk, abc) \right], \quad (27)$$

$$E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a = \frac{1}{16} \sum_{ij, ab} \sum_{kl, cd} a_{ij}^{ab} b_{kl}^{cd} u_{12}(ijkl, abcd), \quad (28)$$

$$E_{QTQ}^{(6)}(\mathrm{II})_b = \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} \frac{u_{11}(ijk, abc) u_{11}(ijk, abc)}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (29)$$

$$E_{QQQ}^{(6)}(\mathrm{II})_b = \frac{1}{(4!)^2} \sum_{ijkl} \sum_{abcd} \frac{u_{12}(ijkl, abcd) u_{12}(ijkl, abcd)}{\epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b - \epsilon_c - \epsilon_d}, \quad (30)$$

$$E_{DTQ}^{(6)}(\mathrm{II}) = \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} \frac{u_7(ijk, abc) u_{11}(ijk, abc)}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (31)$$

$$E_{TTQ}^{(6)}(\mathrm{II}) = \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} \frac{u_8(ijk, abc) u_{11}(ijk, abc)}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}, \quad (32)$$

$$E_{TQQ}^{(6)}(\mathrm{II}) = \frac{1}{(4!)^2} \sum_{ijkl} \sum_{abcd} \frac{u_9(ijkl, abcd) u_{12}(ijkl, abcd)}{\epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l - \epsilon_a - \epsilon_b - \epsilon_c - \epsilon_d}. \quad (33)$$

The calculation of $E(\mathrm{MP6})_{2a_2}$ is clearly more costly than the calculation of $E(\mathrm{MP6})_{2a_1}$, which requires just $O(M^7)$ computational steps. The most expensive terms of $E(\mathrm{MP6})_{2a_2}$ lead to $O(M^9)$ computational steps. Equations (27) and (28) reveal that the T and Q energy denominators disappear. This permits a considerable reduction of the computational cost. For example, the evaluation of $E_{STQ}^{(6)}(\mathrm{II}) + E_{QTQ}^{(6)}(\mathrm{II})_a$ and $E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$ can be reduced from $O(M^7)$ and $O(M^9)$ to no more than $O(M^6)$ steps by using a series of intermediate arrays [see Eqs. (A5)–(A14), (A15)–(A18) and (A19)–(A32) of the Appendix].

$E(\mathrm{MP6})_{2a_3}$ is the only MP6 term, which covers H contributions. However, Eq. (19) does no longer depend on the H energy denominator $(E_0 - E_h)^{-1}$ [1]. The calculation of the energy term $E_{QHQ}^{(6)}$ in Eq. (20) requires just $O(M^6)$ computational steps, which can be shown by separating the term $E_{QHQ}^{(6)}$ $(= E(\mathrm{MP6})_{2a_3})$ into two parts, namely $E_{QHQ}^{(6)}(\mathrm{I})$ and $E_{QHQ}^{(6)}(\mathrm{II})$. $E_{QHQ}^{(6)}(\mathrm{I})$ is give by

$$E_{QHQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)} \right)^\dagger \right]^2 \hat{T}_2^{(1)} \left[\bar{V}_2^1 \left(\hat{T}_2^{(1)} \right)^2 \right]_C \middle| \Phi_0 \right\rangle_C = \frac{1}{4} \sum_{kl} \sum_{cd} a_{kl}^{cd} Q_{kl}^{cd}(u_{10}, a \times a), \quad (34)$$

where we have used the following general notation [6]:

$$Q_{kl}^{cd}(w, a \times b) = \tfrac{1}{8}(2 - \delta_{a,b}) \sum_{mn} \sum_{ef} w(mn, ef) \times \Big\{ a_{kl}^{ef} b_{mn}^{cd} + a_{mn}^{cd} b_{kl}^{ef} - 2 \sum_P (-1)^P P(c/d)(a_{kl}^{ce} b_{mn}^{df} + a_{mn}^{df} b_{kl}^{ce}) - 2 \sum_P (-1)^P P(k/l)(a_{km}^{cd} b_{ln}^{ef} + a_{km}^{ef} b_{ln}^{cd}) + 4 \sum_P (-1)^P P(k/l|c/d) a_{km}^{ce} b_{ln}^{df} \Big\}. \quad (35)$$

Here, w represents any array with four indices m, n and e, f as, for example, $u_{10}(mn, ef)$ or the array of two-electron integrals $\langle mn||ef\rangle$. By comparison of Eqs. (35) and (21), one can see that the computational requirements of $Q_{kl}^{cd}(w, a\times b)$ and $u_{10}(ij, ab)$ are both $O(M^6)$.

The energy term $E_{QHQ}^{(6)}(\mathrm{II})$ is given by

$$
\begin{aligned}
&E_{QHQ}^{(6)}(\mathrm{II}) \\
&= \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left[\overline{V}\frac{1}{3!}\left(\hat{T}_2^{(1)}\right)^3\right]_C \middle| \Phi_0 \right\rangle \\
&= \frac{1}{32}\sum_{ij,ab}\sum_{kl,cd} a_{ij}^{ab} a_{kl}^{cd} \\
&\quad \times \Bigg\{ -\frac{1}{4}\sum_m \sum_P (-1)^P P(i/jkl|ab/cd) \\
&\quad \times \left[\sum_{P'} (-1)^{P'} P'(j/kl) \sum_{n,ef} \langle mn||ef\rangle a_{kl}^{ef} a_{jn}^{cd}\right] a_{im}^{ab} \\
&\quad + \sum_f \sum_p (-1)^P P(ij/kl|a/bcd) \sum_{mn,e} \langle mn||ef\rangle \\
&\quad \times \left[\sum_{P'} (-1)^{P'} P'(k/l|b/cd) a_{mk}^{eb} a_{nl}^{cd} \right. \\
&\quad \left. - \frac{1}{4}\sum_{P'} (-1)^{P'} P'(b/cd) a_{mn}^{cd} a_{kl}^{eb}\right] a_{ij}^{af} \Bigg\}. \qquad (36)
\end{aligned}
$$

As written in Eq. (36), the evaluation of $E_{QHQ}^{(6)}(\mathrm{II})$ involves $O(M^{12})$ operations. However, as shown in the Appendix [Eqs. (A33)–(A42)], the actual cost of calculating $E_{QHQ}^{(6)}(\mathrm{II})$ can be reduced to $O(M^6)$ steps by using 11 intermediate arrays.

Next, we consider Q contributions due to the disconnected cluster operator $\hat{T}_2^{(1)}\hat{T}_2^{(2)}$ which are summarized in $E(\mathrm{MP6})_{2b}$:

$$
\begin{aligned}
&E(\mathrm{MP6})_{2b} \\
&= \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(2)}\right)^\dagger \left(\overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\
&\quad + 2\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle \\
&\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \qquad (37) \\
&= \left[E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I})\right] + 2\left[E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})\right] \\
&\quad + \left[E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I})\right]. \qquad (38)
\end{aligned}
$$

The first term of Eq. (38) can be obtained by

$$
\begin{aligned}
E_{DQD}^{(6)} + E_{DQQ}^{(6)}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(2)}\right)^\dagger \left(\overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\
&= \frac{1}{4}\sum_{kl}\sum_{cd} b_{kl}^{cd} Q_{kl}^{cd}(I, a\times b) \qquad (39)
\end{aligned}
$$

in which I denotes the array of two-electron integrals $\langle mn||ef\rangle$. The calculation of Eq. (39) requires just $O(M^6)$ operations similar as the calculation of $E_{DDQ}^{(6)}$.

The second term in Eq. (38) is given by

$$
\begin{aligned}
&E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I}) \\
&\quad = \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle \\
&\quad = \frac{1}{4}\sum_{ij,ab} a_{ij}^{ab}\left[\frac{1}{4}\sum_{kl,cd} u_9(ijkl, abcd) b_{kl}^{cd}\right]. \qquad (40)
\end{aligned}
$$

Although Eq. (40) contains $u_9(ijkl, abcd)$, which is an $O(M^9)$ term and thereby one of the most expensive terms at sixth-order, introduction of additional intermediate arrays reduces the computation of $E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})$ to $O(M^7)$ operations as is described in the Appendix [Eqs. (A43)–(A49)].

The last term of Eq. (38) is of the form

$$
\begin{aligned}
&E_{QQD}^{(6)} + E_{QQQ}^{(6)}(\mathrm{I}) \\
&\quad = \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \\
&\quad = \left\langle \Phi_0 \middle| \left\{\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\right\}_C \hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle \\
&\qquad + \left\langle \Phi_0 \middle| \left\{\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\right\}_D \hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C, \qquad (41)
\end{aligned}
$$

where the first part $\langle \Phi_0|\{\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\overline{V}\}_C\hat{T}_2^{(1)}\hat{T}_2^{(2)}|\Phi_0\rangle$ is equivalent to $E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$ given in Eq. (28). The second part of Eq. (41) can be evaluated according to

$$
\begin{aligned}
&\left\langle \Phi_0 \middle| \left\{\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \overline{V}\right\}_D \hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \\
&\quad = \left\langle \Phi_0 \middle| \left[\left(\hat{T}_2^{(1)}\right)^\dagger \overline{V}\right]_C \left(\hat{T}_2^{(1)}\right)^\dagger \hat{T}_2^{(1)}\hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \\
&\quad = \frac{1}{4}\sum_{kl}\sum_{cd} a_{kl}^{cd} Q_{kl}^{cd}\left(\tilde{b}_d, a\times b\right), \qquad (42a)
\end{aligned}
$$

with $\tilde{b}_d$ being

$$
\tilde{b}_d = \left\langle \Phi_d \middle| \overline{V}\hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle. \qquad (42b)
$$

In summary, the calculation of the term $E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})$ involves just $O(M^6)$ steps. However, the determination of $E(\mathrm{MP6})_{2b}$ requires $O(M^7)$ operations due to the calculation of the triple amplitudes b^{abc}_{ijk} in the contribution $E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})$.

DERIVATION OF TWO-ELECTRON INTEGRAL FORMULAS FOR $E(\mathrm{MP6})_3$

T effects due to the disconnected T cluster operator $\hat{T}^{(2)}_1\hat{T}^{(1)}_2$ are covered by $E(\mathrm{MP6})_3$, which is given by Eqs. (43) and (44):

$$\begin{aligned} E(\mathrm{MP6})_3 &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_1\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \\ &\quad + 2\left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_2\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \\ &\quad + 2\left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \tfrac{1}{2}\left[\left(\hat{T}^{(1)}_2\right)^\dagger\right]^2 \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \qquad (43) \\ &= \left[E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I})\right] + 2\left[E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})\right] \\ &\quad + 2\left[E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})\right] \\ &\quad + \left[E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})\right]. \qquad (44) \end{aligned}$$

By introducing arrays $u_{13}(i,a)$ and $u_{14}(ij,ab)$ defined by Eqs. (45) and (46),

$$\begin{aligned} u_{13}(i,a) &= \left\langle \Phi^a_i \middle| \left(\overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &= \frac{1}{2}\sum_{mn}\sum_{ef}\langle mn||ef\rangle\left(b^e_i a^{fa}_{mn} - b^a_m a^{ef}_{in} - 2b^e_m a^{af}_{in}\right). \qquad (45) \end{aligned}$$

$$\begin{aligned} u_{14}(ij,ab) &= \left\langle \Phi^{ab}_{ij} \middle| \left(\overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &= \sum_{mn,e}\sum_{p}(-1)^P P(i/j)\langle mn||je\rangle\left(b^e_m a^{ab}_{in} - \tfrac{1}{2}b^e_i a^{ab}_{mn} + b^a_m a^{be}_{in} - b^b_m a^{ae}_{in}\right) \\ &\quad + \sum_{m,ef}\sum_{P}(-1)^P P(a/b)\langle am||ef\rangle\left(b^e_m a^{bf}_{ij} - \tfrac{1}{2}b^b_m a^{ef}_{ij} + b^e_i a^{bf}_{jm} - b^e_j a^{bf}_{im}\right), \qquad (46) \end{aligned}$$

the first two bracket terms in Eq. (44) can be calculated according to Eqs. (47)–(49):

$$\begin{aligned} E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_1\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \\ &= \sum_{i,a} b^a_i u_{13}(i,a). \qquad (47) \end{aligned}$$

$$\begin{aligned} E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_2\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \qquad (48a) \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_2\right)^\dagger \left(\overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_2\right)^\dagger \hat{T}^{(2)}_1 \left(\overline{V}\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \qquad (48b) \\ &= \frac{1}{4}\sum_{ij}\sum_{ab}\left[b^{ab}_{ij}u_{14}(ij,ab) + \tilde{b}^{ab}_{ij}\left(b^a_i b^b_j - b^a_j b^b_i\right)\right]. \qquad (49) \end{aligned}$$

In Eq. (48b), we have used the fact that

$$\begin{aligned} &\left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_2\right)^\dagger \hat{T}^{(2)}_1 \left(\overline{V}\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &\quad = \left\langle \Phi_0 \middle| \left(\hat{T}^{(1)}_2\right)^\dagger \overline{V} \middle| \Phi_d \right\rangle (E_0 - E_d)^{-1} \\ &\qquad \times \left\langle \Phi_d \middle| \hat{T}^{(2)}_1 \left(\overline{V}\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &\quad = \left\langle \Phi_0 \middle| \left(\hat{T}^{(1)}_2\right)^\dagger \overline{V}_2 \left(\hat{T}^{(2)}_1\right)^2 \middle| \Phi_0 \right\rangle. \qquad (50) \end{aligned}$$

Arrays $u_{13}(i,a)$ and $u_{14}(ij,ab)$ appear in the CCSD projection equations [7], which represents an $O(M^6)$ method. Hence, the evaluation of $E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I})$ and $E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})$ requires only $O(M^6)$ operations.

For the last two parts of Eq. (44), namely $E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})$ and $E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})$, the computational cost correspond to $O(M^7)$ and $O(M^6)$. To show this, the $E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})$ is split into three parts:

$$\begin{aligned} E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2 \middle| \Phi_0 \right\rangle_C \qquad (51a) \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \left(\overline{V}\hat{T}^{(2)}_1\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \hat{T}^{(2)}_1 \left(\overline{V}\hat{T}^{(1)}_2\right)_C \middle| \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \hat{T}^{(1)}_2 \left(\overline{V}\hat{T}^{(2)}_1\right)_C \middle| \Phi_0 \right\rangle, \qquad (51b) \end{aligned}$$

where first and last part are evaluated according to Eqs. (52) and (53) using arrays $u_{15}(ijk, abc)$ and $u_{16}(i, a)$ defined in Eqs. (54) and (55), respectively.

$$\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle = \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} b_{ijk}^{abc} u_{15}(ijk, abc), \quad (52)$$

$$\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(1)} \left(\overline{V}\hat{T}_1^{(2)}\right)_C \middle| \Phi_0 \right\rangle = \sum_{i,a} u_{16}(i, a) \tilde{b}_i^a, \quad (53)$$

$$u_{15}(ijk, abc) = \left\langle \Phi_{ijk}^{abc} \middle| \left(\overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle = \sum_P (-1)^P P(a/bc|i/jk) \times \left[\sum_f z_9(i, bc, f) a_{jk}^{af} + \sum_l z_{10}(jk, l, a) a_{il}^{bc} \right], \quad (54)$$

$$u_{16}(i, a) = \frac{1}{4} \sum_{jk} \sum_{bc} b_{ijk}^{abc} a_{jk}^{bc}, \quad (55)$$

with $\tilde{b}_i^a = (\epsilon_i - \epsilon_a) b_i^a$. Arrays $z_9(i, bc, f)$ and $z_{10}(jk, l, a)$ of Eq. (54), which both require $O(M^5)$ operations, are given in Table III.

The second part of Eq. (51b), namely $\langle \Phi_0 | (\hat{T}_3^{(2)})^\dagger \hat{T}_1^{(2)} (\overline{V}\hat{T}_2^{(1)})_C | \Phi_0 \rangle$ can be combined with some part of $E_{TQD}^{(6)} + E_{TQQ}^{(6)}(\mathrm{I})$ [Eq. (40)] as is explained in Eqs. (A43)–(A49) of the Appendix. There, it is also shown that this leads to a reduction of computational cost from $O(M^7)$ to $O(M^6)$. Thus, the most demanding step in the computation of $E_{TTS}^{(6)} + E_{TTQ}^{(6)}(I)$ is the evaluation of $u_{15}(ijk, abc)$ of Eq. (54), which involves $O(M^7)$ steps.

The final term of Eq. (44), $E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I})$, contains two parts:

$$E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I}) = \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \overline{V}\hat{T}_1^{(2)}\hat{T}_2^{(1)} \middle| \Phi_0 \right\rangle_C = \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \hat{T}_2^{(1)} \left(\overline{V}\hat{T}_1^{(2)}\right)_C \middle| \Phi_0 \right\rangle_C + \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \hat{T}_1^{(2)} \left(\overline{V}\hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle_C. \quad (56)$$

The first part of the right side of Eq. (56) adopts the two-electron integral form:

$$\left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \hat{T}_2^{(1)} \left(\overline{V}\hat{T}_1^{(2)}\right)_C \middle| \Phi_0 \right\rangle_C = \left\langle \Phi_0 \middle| \left[\left(\hat{T}_1^{(2)}\right)^\dagger \overline{V} \right]_C \left(\hat{T}_2^{(1)}\right)^\dagger \tfrac{1}{2} \left(\hat{T}_2^{(1)}\right)^2 \middle| \Phi_0 \right\rangle_C = \frac{1}{4} \sum_{kl} \sum_{cd} a_{kl}^{cd} Q_{kl}^{cd}(u_4, a \times a), \quad (57)$$

while the second part can be written as

$$\left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \hat{T}_1^{(2)} \left(\overline{V}\hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle_C = \sum_{l,d} b_l^d u_{17}(l, d), \quad (58)$$

where array $u_{17}(l, d)$ is defined by

$$u_{17}(l, d) = \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \left(\overline{V}\hat{T}_2^{(1)}\right)_C \middle| \Phi_l^d \right\rangle_C. \quad (59)$$

Array $u_{17}(l, d)$ can be evaluated according to Eqs. (A50)–(A57) of the Appendix, where the computational cost is given by $O(M^6)$ operations. Hence, the evaluation of both $E_{QTS}^{(6)} + E_{QTQ}^{(6)}(\mathrm{I})$ and $E_{TTS}^{(6)} + E_{TTQ}^{(6)}(\mathrm{I})$ involves just $O(M^7)$ steps.

DERIVATION OF TWO-ELECTRON INTEGRAL FORMULAS FOR $E(\mathrm{MP6})_4$

The analysis of $E(\mathrm{MP6})_3$ reveals that calculation of the terms resulting from the disconnected T cluster operator $\hat{T}_1\hat{T}_2$ does not lead to higher computational cost than calculation of those terms that result from the connected T operator $\hat{T}_3$. This conclusion also holds in the case of the P cluster operator. In the following, we will demonstrate that the computational requirements of the terms resulting from the disconnected P operator $\hat{T}_2\hat{T}_3$ are not the highest of an $E(\mathrm{MP6})$ calculation since they require just $O(M^8)$ steps.

The P term $E(\mathrm{MP6})_4$ is given by

$$E(\mathrm{MP6})_4 = \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C + \left\langle \Phi_0 \middle| \tfrac{1}{2} \left(\left(\hat{T}_2^{(1)}\right)^\dagger \right)^2 \overline{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C = \left[E_{TPT}^{(6)} + E_{TPQ}^{(6)} \right] + \left[E_{QPT}^{(6)} + E_{QPQ}^{(6)} \right]. \quad (60)$$

For computational reasons, the first bracket term of Eq. (60) is separated into parts I and II:

$$\begin{aligned} E^{(6)}_{TPT} + E^{(6)}_{TPQ} &= \left[E^{(6)}_{TPT}(\mathrm{I}) + E^{(6)}_{TPQ}(\mathrm{I})\right] \\ &\quad + \left[E^{(6)}_{TPT}(\mathrm{II}) + E^{(6)}_{TPQ}(\mathrm{II})\right] \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_D \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle, \end{aligned} \tag{61}$$

which can be calculated according to Eqs. (62) and (63):

$$\begin{aligned} E^{(6)}_{TPT}(\mathrm{I}) + E^{(6)}_{TPQ}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_D \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(1)} \left(\bar{V}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle_C \\ &= \sum_{ia} u_{16}(i,a)u_3(i,a) \end{aligned} \tag{62}$$

and

$$\begin{aligned} E^{(6)}_{TPT}(\mathrm{II}) + E^{(6)}_{TPQ}(\mathrm{II}) &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &= \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} b^{abc}_{ijk} u_{18}(ijk, abc). \end{aligned} \tag{63}$$

Array $u_{18}(ijk, abc)$ of Eq. (63) is given by

$$\begin{aligned} u_{18}(ijk, abc) &= \left\langle \Phi^{abc}_{ijk} \middle| \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &= \frac{1}{4} \sum_{mn} \sum_{ef} \langle mn| \, |ef\rangle \\ &\quad \times \Bigg[\sum_P (-1)^P P(i/jk)\left(b^{abc}_{imn}a^{ef}_{jk} - 2b^{abc}_{jkm}a^{ef}_{in}\right) \\ &\quad + \sum_P (-1)^P P(a/bc)\left(b^{aef}_{ijk}a^{bc}_{mn} - 2b^{bce}_{ijk}a^{af}_{mn}\right) \\ &\quad + \sum_p (-1)^P P(i/jk|a/bc) \\ &\quad \times \left(4b^{bce}_{jkm}a^{af}_{in} - 2b^{ebc}_{imn}a^{af}_{jk} - 2b^{aef}_{mjk}a^{bc}_{in}\right) \Bigg] \\ &= \sum_P (-1)^P P(i/jk) \\ &\quad \times \left[\frac{1}{2} \sum_{mn} z_{11}(mn, jk) b^{abc}_{imn} + \sum_m z_{12}(i, m) b^{abc}_{jkm} \right] \\ &\quad + \sum_p (-1)^P P(a/bc) \\ &\quad \times \left[\frac{1}{2} \sum_{ef} z_{13}(bc, ef) b^{aef}_{ijk} + \sum_e z_{14}(a, e) b^{bce}_{ijk} \right] \\ &\quad + \sum_P (-1)^P P(i/jk|a/bc) \\ &\quad \times \left[\sum_{me} z_{15}(ma, ie) b^{bce}_{jkm} + \sum_f z_{16}(i, bc, f) a^{af}_{jk} \right. \\ &\quad \left. + \sum_n z_{17}(jk, n, a) a^{bc}_{in} \right], \end{aligned} \tag{64}$$

where arrays z_{11}–z_{17} [$\sim O(M^7)$] are defined in Table III. Array $u_{16}(i, a)$ in Eq. (55) requires $O(M^7)$ operations because it depends on the triple amplitudes b^{abc}_{ijk}. Evaluation of $E^{(6)}_{TPT}(\mathrm{I}) + E^{(6)}_{TPQ}(\mathrm{I})$ and $E^{(6)}_{TPT}(\mathrm{II}) + E^{(6)}_{TPQ}(\mathrm{II})$ leads to $O(M^7)$ and $O(M^8)$ steps, respectively.

The second bracket term of Eq. (60) can also be split into two parts:

$$\begin{aligned} E^{(6)}_{QPT} + E^{(6)}_{QPQ} &= \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_D \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &= \left[E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I})\right] \\ &\quad + \left[E^{(6)}_{QPT}(\mathrm{II}) + E^{(6)}_{QPQ}(\mathrm{II})\right]. \end{aligned} \tag{65}$$

In Eq. (65), term I can be calculated according to

$$\begin{aligned} E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I}) &= \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \left(\bar{V}\hat{T}_2^{(1)}\hat{T}_3^{(2)}\right)_D \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \hat{T}_2^{(1)} \left(\bar{V}\hat{T}_3^{(2)}\right)_C \middle| \Phi_0 \right\rangle_C \\ &\quad + \left\langle \Phi_0 \middle| \left[\tfrac{1}{2}\left[\left(\hat{T}_2^{(1)}\right)^\dagger\right]^2 \hat{T}_3^{(2)} \left(\bar{V}\hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle_C \end{aligned} \tag{66a}$$

$$= \frac{1}{4} \sum_{kl} \sum_{cd} a^{cd}_{kl} Q^{cd}_{kl}(u_6, a \times a) + \sum_{i,a} \tilde{b}^a_i u_{19}(i, a), \tag{66b}$$

where array $u_{19}(i,a)$ is determined by

$$u_{19}(i,a) = \sum_{j,b} a_{ij}^{ab} u_{16}(j,b) - \frac{1}{2} \sum_{j,cb} a_{ij}^{cb} z_{18}(j,a,bc), \quad (67)$$

using intermediate array $z_{18}(j,a,bc)$, which represents contractions of the triple amplitudes b_t with the double amplitudes a_d (see Table III). Accordingly, the computational requirements for the calculation of $E_{QPT}^{(6)}(\mathrm{I}) + E_{QPQ}^{(6)}(\mathrm{I})$ are determined by the evaluation of the triple amplitudes b_t [$\sim O(M^7)$].

The second bracket of Eq. (65) is given by

$$E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II}) = \left\langle \Phi_0 \left| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)} \right)^\dagger \right]^2 \left(\bar{V} \hat{T}_2^{(1)} \hat{T}_3^{(2)} \right)_C \right| \Phi_0 \right\rangle = \frac{1}{32} \sum_{ij,ab} \sum_{kl,cd} a_{ij}^{ab} a_{kl}^{cd} u_{20}(ijkl,abcd), \quad (68)$$

where array $u_{20}(ijkl,abcd)$ is defined by

$$\begin{aligned} u_{20}(ijkl,abcd) &= \left\langle \Phi_{ijkl}^{abcd} \left| \left(\bar{V} \hat{T}_2^{(1)} \hat{T}_3^{(2)} \right)_C \right| \Phi_0 \right\rangle \\ &= \sum_P (-1)^P P(ab/cd|k/ijl) \sum_f \sum_{P'} (-1)^{P'} \\ &\quad \times P'(c/d) \sum_{me} \langle md||ef\rangle a_{km}^{ce} b_{ijl}^{abf} \\ &\quad - \sum_P (-1)^P P(c/abd|ij/kl) \sum_m \sum_{P'} (-1)^{P'} \\ &\quad \times P'(k/l) \sum_{nf} \langle mn||lf\rangle a_{kn}^{cf} b_{ijm}^{abd} \\ &\quad - \sum_P (-1)^P P(ab/cd|i/jkl) \\ &\quad \times \sum_m \left(\frac{1}{2} \sum_{ef} \sum_{P'} (-1)^{P'} P'(c/d) \langle md||ef\rangle b_{jkl}^{ecf} \right. \\ &\quad \left. + \sum_{P'} (-1)^{P'} P'(l/jk) \sum_{nf} \langle mn||lf\rangle b_{jkn}^{fcd} \right) a_{im}^{ab} \\ &\quad + \sum_P (-1)^P P(a/bcd|ij/kl) \\ &\quad \times \sum_f \left(\sum_{P'} (-1)^{P'} P'(d/bc) \sum_{me} \langle md||ef\rangle b_{klm}^{bce} \right. \\ &\quad \left. + \frac{1}{2} \sum_{mn} \sum_{P'} (-1)^{P'} P'(k/l) \langle mn||lf\rangle b_{kmn}^{cdb} \right) a_{ij}^{af} \\ &\quad - \frac{1}{2} \sum_P (-1)^P P(ab/cd|l/ijk) \\ &\quad \times \sum_{mn} \langle mn||lf\rangle a_{mn}^{cd} b_{ijk}^{abf} \\ &\quad - \frac{1}{2} \sum_P (-1)^P P(d/abc|ij/kl) \\ &\quad \times \sum_{ef} \langle md||ef\rangle a_{ij}^{ef} b_{klm}^{cab}. \end{aligned} \quad (69)$$

Since the evaluation of $u_{20}(ijkl,abcd)$ involves $O(M^{11})$ steps, one has to use intermediate arrays to reduce the computational cost for the evaluation of $E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$. In the Appendix [Eqs. (A58)–(A80)] it is described that $E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$ can be split into four parts, each of which can be evaluated in no more than $O(M^8)$ computational steps using several intermediate arrays.

Implementation of a MP6 Computer Program

In the previous section, we derived two-electron integral formulas for all 36 MP6 energy terms grouped into the four energy parts $E(\mathrm{MP6})_1$, $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$. The most expensive terms [$\geq O(M^8)$] that have to be calculated to obtain the energy $E(\mathrm{MP6})$ are summarized in Table IV.

In each case, we have checked how by the use of intermediate arrays the computational cost can be reduced to a minimum, and we have found that this can be done for all the disconnected cluster operator terms associated with T, Q, or P excita-

TABLE IV
MP6 energy contributions requiring high computational cost.

	Energy contribution	Expression	Cost
$E(\mathrm{MP6})_1$	$E_{DTT}^{(6)}$	Eq. (11)	$O(M^8)$
	$E_{TTT}^{(6)}$	Eq. (12)	$O(M^8)$
	$E_{TQT}^{(6)}$	Eq. (13)	$O(M^9)$
$E(\mathrm{MP6})_{2a_2}$	$E_{QQQ}^{(6)}(\mathrm{II})_b$	Eq. (30)	$O(M^9)$
	$E_{TTQ}^{(6)}(\mathrm{II})$	Eq. (32)	$O(M^8)$
	$E_{TQQ}^{(6)}(\mathrm{II})$	Eq. (33)	$O(M^9)$
$E(\mathrm{MP6})_4$	$E_{TPT}^{(6)}(\mathrm{II}) + E_{TPQ}^{(6)}(\mathrm{II})$	Eq. (63)	$O(M^8)$
	$E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$	Eq. (68)	$O(M^8)$

tions in $E(\mathrm{MP6})_2$, $E(\mathrm{MP6})_3$, and $E(\mathrm{MP6})_4$. However, in some cases it is of advantage to combine the calculation of disconnected cluster operator terms with that of related connected cluster operator terms involving a higher cost factor rather than calculating each MP6 term individually. In this way, superfluous input/output (I/O) operations are suppressed in exchange of a slight increase in computational cost. We have found that in this way the calculation of $E(\mathrm{MP6})$ becomes much more efficient.

In Table V, all MP6 energy contributions are listed in the sequence they are calculated within the *ab initio* program package COLOGNE94 [8]. First, the double amplitudes a_d from a MP2 calculation are used to calculate the second-order amplitudes b_x ($x = s, d, t$) according to Eqs. (A2)–(A4) of the Appendix. Utilizing first- and second-order amplitudes, the terms $E^{(6)}_{QPT}(\mathrm{II}) + E^{(6)}_{QPQ}(\mathrm{II})$ [Eq. (68)], $E^{(6)}_{QHQ}(\mathrm{II})$ [Eq. (36)], $E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$ [Eq. (27)], $E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})$ [Eq. (42)] of steps 1 and 2 as well as some matrix elements for $E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QTQ}(\mathrm{I})$ [Eq. (66)] of step 3 (Table V) are calculated. Next, array u_8 is determined, which has to be available for carrying out the loop over T excitations, which leads to the calculation of $E^{(6)}_{DTT}$ [Eq. (11)] and $E^{(6)}_{TTT}$ [Eq. (12)] in step 4 and requires $O(M^8)$ operations. Although less costly, contributions $E^{(6)}_{DTS}$, $E^{(6)}_{DTQ}(\mathrm{I})$, $E^{(6)}_{TTS}$, $E^{(6)}_{TTQ}(\mathrm{I})$, and $E^{(6)}_{DTD}$ are calculated at the same time. In this way the MP6 program is simplified and separated calculations involving a large amount of I/O avoided.

In step 5, the two contributions $E^{(6)}_{DQD}$ [Eq. (39)] and $E^{(6)}_{DQQ}(\mathrm{I})$ [Eq. (39)] are computed. Computationally most demanding is step 6, in which one has to loop over all Q excitations to evaluate the $O(M^9)$ terms $E^{(6)}_{TQT}$ [Eq. (13)], $E^{(6)}_{TQQ}(\mathrm{II})$ [Eq. (33)], and $E^{(6)}_{QQQ}(\mathrm{II})_b$ [Eq. (30)]. In the Q loop, also some less costly terms such as $E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a$ [Eq. (28)] and $E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})$ [Eq. (40)] are calculated to reduce extensive I/O operations. Step 7 leads to $E^{(6)}_{DTQ}(\mathrm{II})$ [Eq. (31)] and $E^{(6)}_{TTQ}(\mathrm{II})$ [Eq. (32)], where calculation of the latter term also requires $O(M^8)$ operations. The evaluation of a number of MP6 contributions requires just $O(M^7)$ or less computational steps. Actually, determination of these terms can be connected with the calculation of appropriate MP5 terms [6, 9], which leads to a clear structuring of steps 10–19. In step 22, the last $O(M^8)$ term, $E^{(6)}_{TPT}(\mathrm{II}) + E^{(6)}_{TPQ}(\mathrm{II})$ [Eq. (63)], is evaluated. The calculation of $E(\mathrm{MP6})$ is finished by complementing energy contributions $E^{(6)}_{QTQ}(\mathrm{II})_b$ [Eq. (29)] and $E^{(6)}_{QTS}$ [Eq. (58)] in steps 23 and 24.

We have set up a MP6 program in such a way that it can also be run with a program package such as Gaussian [10]. In addition, we have programmed somewhat modified routes to $E(\mathrm{MP6})$, which are needed for testing purposes (see below) or which help to evaluate partial contributions to the MP6 correlation energy.

Testing and Application of the MP6 Computer Program

Computer codes such as the MP6 program are rather complicated although they are set up in the same way as lower-order MPn programs have been set up [6, 9, 10]. Beside the actual development work, the programming work, and the work necessary to reduce run times of the MP6 program, it is a major part of the work and in the end most time consuming to make sure that the final computer codes are free of errors. We have used three different ways of checking the MP6 computer programs.

First, we have compared calculated $E(\mathrm{MP6})$ values with results from full configuration interaction (FCI) calculations. These authors have shown that high-order MPn energies (up to $n = 48$) can be obtained from FCI calculations published by Handy and co-workers [11, 12]. In this way, FCI-based MP6 energies (FCI–MP6) have been calculated for a number of small electron systems including $H_2O, {}^1A_1$, ($R_e = 0.967$ Å, $\theta = 107.6°$), $NH_2, {}^2B_1$, both at equilibrium geometry ($R_e = 1.013$ Å, $\omega = 103.2°$) and at "stretched geometries" with $1.5R_e$ and $2R_e$, $BH, {}^1\Sigma_g$ ($R_e = 1.232$ Å), $Be_2, {}^1\Sigma_g^+$ ($R_e = 5.25$ Å), $CH_2, {}^1A_1$ ($R_e = 1.102$ Å, $\theta = 104.7°$), and $CN, {}^2\Sigma^+$ ($R_e = 1.1619$ Å). In Table VI, FCI–MPn energies for $n = 2, 3, 4, 5, 6$ from the work of Handy and co-workers [11, 12] are listed and compared with the corresponding MPn energies obtained in this work. Lower orders than $n = 6$ are included into the comparison to identify differences in energy caused by geometries or other computational differences that may result from the limited information possible in a publication.

For all electron systems listed in Table VI, calculated MP6 correlation energy contributions agree with the corresponding FCI–MP6 values within 10^{-6} hartree, which is also the difference between many of the lower-order correlation contributions.

TABLE V
Implementation of the MP6 program.

Step	Required arrays and comments	Expression	Calculated MP6 contributions	Expression
1	a_d and b_t	Eqs. (A1) and (A4)	$E^{(6)}_{QPT}(\mathrm{II}) + E^{(6)}_{QPQ}(\mathrm{II})$, $E^{(6)}_{QlIQ}(\mathrm{II})$	Eqs. (A58)–(A80) and (A33)–(A42)
2	a_d, b_s, and b_d	Eqs. (A1)–(A3)	$E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$	Eqs. (A15)–(A18)
			$\langle\Phi_0\vert\{\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\bar{V}\}_D\hat{T}_2^{(1)}\hat{T}_2^{(2)}\vert\Phi_0\rangle_C$ in $E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})$	Eq. (42)
3	a_d and b_t	Eqs. (A1) and (A4)	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_3^{(2)}(\bar{V}\hat{T}_2^{(1)})_C\vert\Phi_0\rangle$ in $E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I})$	Eq. (66b)
4	b_s, b_d, b_t, and u_8. The T loop is carried out	Eqs. (A2)–(A4), and Table I	$E^{(6)}_{DTT}$ and $E^{(6)}_{TTT}$	Eqs. (11) and (12)
			$E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})$	Eq. (48a)
			$E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})$	Eq. (51a)
			$E^{(6)}_{DTD}$	Table II
5	a_d and b_d	Eqs. (A1) and (A3)	$E^{(6)}_{DQD} + E^{(6)}_{DQQ}(\mathrm{I})$	Eq. (39)
6	u_9	Table I	$E^{(6)}_{TQT}$ and $E^{(6)}_{TQQ}(\mathrm{II})$	Eqs. (13) and (33)
	u_{12}	Eq. (26)	$E^{(6)}_{QQQ}(\mathrm{II})_b$	Eq. (30)
	a_d and b_d	Eqs. (A1) and (A3)	$E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a$	Eqs. (A19)–(A32)
	The Q loop is carried out		$E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})$	Eq. (40)
7	u_7, u_8, and u_{11}	Table I and Eq. (25)	$E^{(6)}_{DTQ}(\mathrm{II})$ and $E^{(6)}_{TTQ}(\mathrm{II})$	Eqs. (31) and (32)
8	b_s and u_{13}	Eqs. (A2) and (45)	$E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I})$	Eq. (47)
9	a_d and u_{10}	Eqs. (A1) and (22)	$E^{(6)}_{QlIQ}(\mathrm{I})$	Eq. (34)
	Calculation of steps 10–19 is based on MP5			
10	u_5 and u_{10}	Table I and Eq. (22)	$E^{(6)}_{DDD}$ and $E^{(6)}_{DDQ}$	Table II and Eq. (16)
11	u_1 and u_2	Table I	$E^{(6)}_{SSD}$ and $E^{(6)}_{DSD}$	Table II
12	u_5 and u_4	Table I	$E^{(6)}_{SDD}$	Table II
13	u_5, u_6; u_2, u_3	Table I	$E^{(6)}_{DDT}$ and $E^{(6)}_{DST}$	Table II
14	u_1 and u_{10}	Table I and Eq. (22)	$E^{(6)}_{SSS}$ and $E^{(6)}_{QDQ}$	Table II and Eq. (16)
15	u_1, u_3; u_6, u_{10}	Table I and Eq. (22)	$E^{(6)}_{SST}$ and $E^{(6)}_{TDQ}$	Table II and Eq. (16)
16	u_4 and u_{10}	Table I and Eq. (22)	$E^{(6)}_{SDS}$ and $E^{(6)}_{SDQ}$	Table II and Eq. (23)
17	a_d and u_4	Eq. (A1) and Table I	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_2^{(1)}(\bar{V}\hat{T}_1^{(2)})_C\vert\Phi_0\rangle_C$ for $E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})$	Eq. (57)
18	u_4 and u_6	Table I	$E^{(6)}_{SDT}$ and $E^{(6)}_{TDT}$	Table II
19	u_3	Table I	$E^{(6)}_{TST}$	Table II
20	a_d and u_6	Eq. (A1) and Table I	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_2^{(1)}(\bar{V}\hat{T}_3^{(2)})_C\vert\Phi_0\rangle$ for $E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I})$	Eq. (66b)
21	u_3 and u_{16}	Table I and Eq. (55)	$E^{(6)}_{TPT}(\mathrm{I}) + E^{(6)}_{TPQ}(\mathrm{I})$	Eq. (62)
22	b_t and u_{18}	Eqs. (A4) and (64)	$E^{(6)}_{TPT}(\mathrm{II}) + E^{(6)}_{TPQ}(\mathrm{II})$	Eq. (63)
23	u_{11}	Eq. (25)	$E^{(6)}_{QTQ}(\mathrm{II})_b$	Eq. (29)
24	b_s and u_{17}	Eqs. (A2) and (59)	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_1^{(2)}(\bar{V}\hat{T}_2^{(1)})_C\vert\Phi_0\rangle_C$ for $E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})$	Eq. (58)

TABLE VI

Comparison of directly calculated MP*n* energies (*n* = 1, 2, 3, 4, 5, and 6) with MP*n* energies from full CI (FCI) calculations for some small electron systems (all energies in hartree)

	$E^{(n)}$	MP*n*	MP*n*–FCI		$E^{(n)}$	MP*n*	MP*n*–FCI
1)	H_2O, $^1A_1$,	R_e = 0.967 Å,	θ = 107.6°, 6-21G Basis	5)	NH_2, $^2B_1$,	1.5 R_e,	θ = 103.2°, 6-31G
	E(HF)	−75.888432	−75.888430		E(HF)	−55.405143	−55.405143
	$E^{(2)}$	−0.120897	−0.120865		$E^{(2)}$	−0.062116	−0.062116
	$E^{(3)}$	−0.003302	−0.003303		$E^{(3)}$	−0.011394	−0.011394
	$E^{(4)}$	−0.004856	−0.004849		$E^{(4)}$	−0.008695	−0.008695
	$E^{(5)}$	−0.000488	−0.000488		$E^{(5)}$	−0.005776	−0.005776
	$E^{(6)}$	−0.000436	−0.000435		$E^{(6)}$	−0.004888	−0.004887
2)	BH, $^1\Sigma^+$	R_e = 1.232 Å,	[4*s*2*p*1*d*/2*s*1*p*] Basis	6)	NH_2, $^2B_1$,	2.0 R_e,	θ = 103.2°, 6-31G
	E(HF)	−25.125260	−25.125260		E(HF)	−55.381931	−55.381931
	$E^{(2)}$	−0.060333	−0.060297		$E^{(2)}$	−0.031539	−0.031539
	$E^{(3)}$	−0.016472	−0.016482		$E^{(3)}$	−0.006208	−0.006208
	$E^{(4)}$	−0.005925	−0.005924		$E^{(4)}$	−0.002508	−0.002508
	$E^{(5)}$	−0.002540	−0.002540		$E^{(5)}$	−0.001234	−0.001234
	$E^{(6)}$	−0.001228	−0.001226		$E^{(6)}$	−0.000845	−0.000846
3)	CH_2, $^1A_1$	R_e = 1.102 Å,	θ = 104.7° [4*s*2*p*1*d*/2*s*1*p*]	7)	Be_2 $^1\Sigma_g^+$	R_e = 5.25 Å	7*s*3*p*1*d* Basis
	E(HF)	−38.876360	−38.876358		E(HF)	−29.138980	−29.138980
	$E^{(2)}$	−0.092785	−0.092657		$E^{(2)}$	−0.061091	−0.061081
	$E^{(3)}$	−0.017902	−0.017926		$E^{(3)}$	−0.020766	−0.020769
	$E^{(4)}$	−0.005481	−0.005476		$E^{(4)}$	−0.009118	−0.009118
	$E^{(5)}$	−0.002017	−0.002018		$E^{(5)}$	−0.004283	−0.004283
	$E^{(6)}$	−0.000973	−0.000973		$E^{(6)}$	−0.002101	−0.002107
4)	NH_2, $^2B_1$,	R_e = 1.013 Å,	θ = 103.2°, 6-31G	8)	CN $^2\Sigma^+$	R_e = 1.1619 Å	STO-3G Basis
	E(HF)	−55.532248	−55.532248		E(HF)	−91.01943	−91.01943
	$E^{(2)}$	−0.085512	−0.085512		$E^{(2)}$	−0.09469	−0.09469
	$E^{(3)}$	−0.009815	−0.009815		$E^{(3)}$	−0.00792	−0.00792
	$E^{(4)}$	−0.003612	−0.003613		$E^{(4)}$	−0.01335	−0.01335
	$E^{(5)}$	−0.001192	−0.001192		$E^{(5)}$	−0.00683	−0.00683
	$E^{(6)}$	−0.000464	−0.000463		$E^{(6)}$	−0.00633	−0.00634

Although the agreement between FCI–MP6 and our MP6 data seems to suggest reliability of the new MP6 program, it does not prove that the latter is without any errors. Since all test molecules are rather small possessing just a limited number of electrons, higher excitations such as P or H do not contribute significantly to the final correlation energy. As a consequence, any errors in these terms do not show up in the comparison between FCI–MP6 and MP6 energies. This also holds for any other low-value term and has to be considered in the testing. Therefore, we have used additional procedures to check calculated MP6 results. For example, we have programmed large parts of the MP6 routines in an alternative way, which is documented in Table VII.

In the case of the energy terms associated with disconnected cluster operators (see 1 in Table VII), we have programmed alternative procedures that do not take advantage of intermediate arrays and, therefore, are much more costly. For example, we have directly evaluated contributions such as $E^{(6)}_{QHQ}$(II) and $E^{(6)}_{QPT}$(II) + $E^{(6)}_{QPQ}$(II) by using Eqs. (36) and (68) rather than the appropriate equations in the Appendix [(A33)–(A42), (A58)–(A80)] that are based on intermediate arrays. In the case of $E^{(6)}_{STS}$ + $E^{(6)}_{STQ}$(I), $E^{(6)}_{TTS}$ + $E^{(6)}_{TTQ}$(I), $E^{(6)}_{QTS}$ + $E^{(6)}_{QTQ}$(I) and $E^{(6)}_{TPT}$ + $E^{(6)}_{TPQ}$, alternatives to those equations given in the text (see Table VII) are given in Eqs. (70)–(73):

$$E^{(6)}_{STS} + E^{(6)}_{STQ}(I) = \left\langle \Phi_0 \middle| \overline{V} \left[\left(\hat{T}_1^{(2)}\right)^\dagger \hat{T}_1^{(2)} \hat{T}_2^{(1)} \right]_C \middle| \Phi_0 \right\rangle + \left\langle \Phi_0 \middle| \overline{V} \left[\left(\hat{T}_1^{(2)}\right)^\dagger \hat{T}_2^{(1)} \right]_C \hat{T}_1^{(2)} \middle| \Phi_0 \right\rangle_C \quad (70)$$

TABLE VII
Checking of the MP6 program.[a]

Checking possibility	Energy terms checked	Comments
1. Programming of alternative formulas		
Eq. (28) vs. Eqs. (A19)–(A32)	$E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a$	Checking of the Q loop
Eq. (27) vs. Eqs. (A15)–(A18)	$E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$	
Eq. (36) vs. Eqs. (A33)–(A42)	$E^{(6)}_{QHQ}(\mathrm{II})$	Calculations are carried
Eq. (47) vs. Eq. (70)	$E^{(6)}_{STS} + E^{(6)}_{STQ}(\mathrm{I})$	out with and without
Eq. (51b) vs. Eq. (71)	$E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I})$	intermediate arrays
Eqs. (57)–(58) vs. Eq. (72)	$E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I})$	
Eqs. (62)–(63) vs. Eq. (73)	$E^{(6)}_{TPT} + E^{(6)}_{TPQ}$	
Eq. (66a) vs. Eq. (66b)	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_3^{(2)}(\bar{V}\hat{T}_2^{(1)})_C\vert\Phi_0\rangle_C$ for $E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I})$	
Eq. (68) vs. Eqs. (A58)–(A80)	$E^{(6)}_{QPT}(\mathrm{II}) + E^{(6)}_{QPQ}(\mathrm{II})$	
2. Use of MP5 results: First-order cluster operators lead to MP5 terms, which can directly be checked.		
		MP5 term(s) used for checking
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in Eq. (16)	$E^{(6)}_{DDQ}$	$E^{(5)}_{DQ}$
$(\hat{T}_2^{(2)})^\dagger$ replaced by $(\hat{T}_2^{(1)})^\dagger$ in Eq. (39)	$E^{(6)}_{DQD} + E^{(6)}_{DQQ}(\mathrm{I})$	$E^{(5)}_{QD} + E^{(5)}_{QQ}(\mathrm{I})$
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in Eq. (40)	$E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})$	$2E^{(5)}_{TQ}$
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in Eq. (41)	$E^{(6)}_{QQD} + E^{(6)}_{QQQ}(\mathrm{I})$	$2E^{(5)}_{QQ}$
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in Eq. (48a)	$E^{(6)}_{DTS} + E^{(6)}_{DTQ}(\mathrm{I})$	$E^{(5)}_{TS} + E^{(5)}_{TQ}(\mathrm{I})$
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in u_7 of Eq. (31)	$E^{(6)}_{DTQ}(\mathrm{II})$	$E^{(5)}_{TQ}(\mathrm{II})$
$\hat{T}_2^{(2)}$ replaced by $\hat{T}_2^{(1)}$ in u_2, u_5,	$E^{(6)}_{SSD}$, $E^{(6)}_{DSD}$, $E^{(6)}_{DST}$, and $E^{(6)}_{SDD}$	$E^{(5)}_{SS}$ and $E^{(5)}_{SD}$ and $E^{(5)}_{ST}$
and u_7 of Tables I and II	$E^{(6)}_{DDD}$, $E^{(6)}_{DDT}$ and $E^{(6)}_{DTD}$, $E^{(6)}_{DTT}$	$E^{(5)}_{SD}$, $E^{(5)}_{DD}$, $E^{(5)}_{DT}$, and $E^{(5)}_{TT}$
$\frac{u_1(i,a)}{\Delta_i^a}$ [or $\frac{u_3(i,a)}{\Delta_i^a}$] replaced by b_i^a in Table II	$E^{(6)}_{SSS}$ and $E^{(6)}_{SST}$ (or $E^{(6)}_{TST}$)	$E^{(5)}_{SS}$ and $E^{(5)}_{ST}$
$\frac{u_4(ij,ab)}{\Delta_{ij}^{ab}}$ [or $\frac{u_6(ij,ab)}{\Delta_{ij}^{ab}}$] replaced by b_{ij}^{ab} in Table II	$E^{(6)}_{SDS}$ and $E^{(6)}_{SDT}$ (or $E^{(6)}_{TDT}$)	$E^{(5)}_{SD}$ and $E^{(5)}_{DT}$
$\frac{u_8(ijk,abc)}{\Delta_{ijk}^{abc}}$ replaced by b_{ijk}^{abc} in Table II	$E^{(6)}_{TTT}$	$E^{(5)}_{TT}$
$\frac{u_9(ijkl,abcd)}{\Delta_{ijkl}^{abcd}}$ replaced by $\frac{1}{2}a_{ij}^{ab}a_{kl}^{cd}$ in Table II	$E^{(6)}_{TQT}$	$E^{(5)}_{QT}$
$\frac{u_4(ij,ab)}{\Delta_{ij}^{ab}}$ [or $\frac{u_{10}(ij,ab)}{\Delta_{ij}^{ab}}$] replaced by b_{ij}^{ab} in Eq. (23)	$E^{(6)}_{SDQ}$	$E^{(5)}_{SD}$ (or $E^{(5)}_{DQ}$)
$\frac{u_6(ij,ab)}{\Delta_{ij}^{ab}}$ [or $\frac{u_{10}(ij,ab)}{\Delta_{ij}^{ab}}$] replaced by b_{ij}^{ab} similar to Eq. (23)	$E^{(6)}_{TDQ}$ and $E^{(6)}_{QDQ}$	$E^{(5)}_{DQ}$
$\frac{u_{11}(ijk,abc)}{\Delta_{ijk}^{abc}}$ replaced by b_{ijk}^{abc} in Eq. (29)	$E^{(6)}_{QTQ}(\mathrm{II})_b$	$E^{(5)}_{TQ}(\mathrm{II})$
$\frac{u_{11}(ijk,abc)}{\Delta_{ijk}^{abc}}$ replaced by b_{ijk}^{abc} in Eq. (32)	$E^{(6)}_{TTQ}(\mathrm{II})$	$E^{(5)}_{TT}$
$u_{12}(ijkl,abcd)$ replaced by $\frac{1}{2}a_{ij}^{ab}a_{kl}^{cd}$ in Eqs. (30) and (33)	$E^{(6)}_{QQQ}(\mathrm{II})_b$ and $E^{(6)}_{TQQ}(\mathrm{II})$	$E^{(5)}_{QQ}(\mathrm{II})$ and $E^{(5)}_{TQ}$
$u_{10}(ij,ab)$ replaced by $\langle ij\vert\vert ab\rangle$ in Eq. (34)	$E^{(6)}_{QHQ}(\mathrm{I})$	$E^{(4)}_{Q}$
$\bar{V}\hat{T}_3^{(2)}$ replaced by $\bar{V}\hat{T}_2^{(1)}$ in Eq. (66a)	$\langle\Phi_0\vert\frac{1}{2}[(\hat{T}_2^{(1)})^\dagger]^2\hat{T}_2^{(1)}(\bar{V}\hat{T}_3^{(2)})_C\vert\Phi_0\rangle_C$ for $E^{(6)}_{QPT}(\mathrm{I}) + E^{(6)}_{QPQ}(\mathrm{I})$	$E^{(5)}_{QQ}(\mathrm{I})$

[a] In each case, calculated energy terms differed by not more than 10^{-10} hartree.

$$E^{(6)}_{TTS} + E^{(6)}_{TTQ}(\mathrm{I}) = \left\langle \Phi_0 \middle| \left[\left(\hat{T}^{(2)}_3\right)^\dagger \overline{V} \right]_C \hat{T}^{(1)}_2 \hat{T}^{(2)}_1 \middle| \Phi_0 \right\rangle. \quad (71)$$

$$E^{(6)}_{QTS} + E^{(6)}_{QTQ}(\mathrm{I}) = \left\langle \Phi_0 \middle| \left\{ \tfrac{1}{2} \left[\left(\hat{T}^{(1)}_2\right)^\dagger \right]^2 \overline{V} \right\}_C \hat{T}^{(2)}_2 \hat{T}^{(2)}_1 \middle| \Phi_0 \right\rangle + \left\langle \Phi_0 \middle| \left[\left(\hat{T}^{(1)}_2\right)^\dagger \overline{V} \right]_C \left[\left(\hat{T}^{(1)}_2\right)^\dagger \hat{T}^{(1)}_2 \hat{T}^{(2)}_1 \right]_C \middle| \Phi_0 \right\rangle. \quad (72)$$

$$E^{(6)}_{TPT} + E^{(6)}_{TPQ} = \sum_p^P \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \overline{V} \middle| \Phi_p \right\rangle (E_0 - E_p)^{-1} \times \left[\left\langle \Phi_p \middle| \overline{V} \hat{T}^{(2)}_3 \middle| \Phi \right\rangle + \left\langle \Phi_p \middle| \hat{T}^{(1)}_2 \left(\overline{V} \hat{T}^{(1)}_2 \right)_C \middle| \Phi_0 \right\rangle \right] - E(\mathrm{MP2}) \left\langle \Phi_0 \middle| \left(\hat{T}^{(2)}_3\right)^\dagger \hat{T}^{(2)}_3 \middle| \Phi_0 \right\rangle. \quad (73)$$

A program part tested in this way was considered to be correct if the difference in energy values obtained by different programs is smaller or equal to 10^{-10} hartree.

A second way of efficiently searching for errors in the MP6 program is to replace second-order amplitudes by the appropriate first-order amplitudes to get the corresponding fifth-order energy contributions, which can be directly compared with existing MP5 results [9, 13]. As shown in Table VII, this procedure is straightforward and can be extended to (partial) third-order amplitudes to be replaced by second-order amplitudes or products of first-order amplitudes. In each case, it was verified that the energy contributions obtained at MP5 did not differ from the corresponding directly calculated MP5 terms by more than 10^{-10} hartree. After checking all MP6 energy contributions in the various ways listed in Table VII, we concluded that MP6 program and MP6 energies described in this work are reliable. The MP6 program was installed on a CRY Y-MP to be run within the ab initio package COLOGNE94 [8].

Conclusions

In the present work, we have described the implementation of a MP6 program for routine calculations. For this purpose, we have developed two-electron integral formulas for all MP6 energy contributions starting from the cluster operator formulation of MP6 discussed in the first article of this series [1]. Particular care has been taken to reduce computational cost by introducing intermediate arrays in connection with the calculation of contributions resulting from disconnected cluster operator terms. In this way, the actual computational cost have been reduced from maximally $O(M^{12})$ to maximally $O(M^9)$. The four energy terms which lead to this cost factor are the terms calculated in the Q loop of the program (Table V). The second largest cost factor is presented by the terms calculated in the T loop. For the reason of reducing I/O operations some of the cheaper operations are integrated into the T and Q loops although this leads to somewhat higher computational cost.

Based on the integral formulas presented in this work, a MP6 program for routine calculations has been developed and implemented on a CRAY Y-MP. The reliability of calculated MP6 correlation energies has been checked by a three-pronged approach: First, MP6 benchmark calculations have been carried out for 8 different electron systems, for which a decomposition of FCI results in terms of MPn correlation energies are available [11, 12]. MP6 and MP6–FCI results agree within 10^{-6} hartree, which gives indication that MP6 energies calculated in this work are reliable. However, final proof for the reliability of calculated MP6 energies is obtained by carrying out two additional testing possibilities. These involve the development of alternative program versions. Hence, in the second step, we have programmed energy contributions that result from disconnected cluster operators without the use of intermediate arrays thus leading to computationally more demanding program versions. The remaining sixth-order contributions have been checked by taking advantage of relationships between fifth-order and sixth-order energy contributions. In all cases, MP6 energies were found to be accurate up to 10^{-10} hartree suggesting that all terms checked in this way are correctly programmed. First applications of the MP6 method have been presented. A more detailed account of calculated MP6 correlation energies will be given in the third part of this series [2].

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Appendix

The evaluation of terms such as $E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$, $E^{(6)}_{DQQ}(\mathrm{II}) + E^{(6)}_{QQQ}(\mathrm{II})_a$, $E^{(6)}_{QHQ}(\mathrm{II})$, $E^{(6)}_{TQD} + E^{(6)}_{TQQ}(\mathrm{I})$ and $E^{(6)}_{QPT}(\mathrm{II}) + E^{(6)}_{QPQ}(\mathrm{II})$, etc., can be simplified by using intermediate arrays. To demonstrate this, we first introduce appropriate formulas for first-order and second-order amplitudes a^{ab}_{ij}, b^{a}_{i}, b^{ab}_{ij}, and b^{abc}_{ijk}, respectively, in terms of two-electron integrals over spin orbitals.

$$a^{ab}_{ij} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}\langle ab||ij\rangle. \quad \text{(A1)}$$

$$b^{a}_{i} = -(\epsilon_i - \epsilon_a)^{-1} \times\left[\frac{1}{2}\sum_{m,ef}\langle ma||ef\rangle a^{ef}_{im} + \frac{1}{2}\sum_{mn,e}\langle mn||ie\rangle a^{ae}_{mn}\right]. \quad \text{(A2)}$$

$$b^{ab}_{ij} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1} \times\left[\frac{1}{2}\left(\sum_{ef}\langle ab||ef\rangle a^{ef}_{ij} + \sum_{mn}\langle mn||ij\rangle a^{ab}_{mn}\right) - \sum_{me}\sum_{P}(-1)^P P(i/j|a/b)\langle mb||je\rangle a^{ae}_{im}\right]. \quad \text{(A3)}$$

$$b^{abc}_{ijk} = (\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c)^{-1} \times\sum_{P}(-1)^P P(i/jk|a/bc) \times\left[\sum_{e}\langle bc||ei\rangle a^{ae}_{jk} - \sum_{m}\langle ma||jk\rangle a^{bc}_{im}\right]. \quad \text{(A4)}$$

In addition, we introduce the intermediate arrays x_1–x_{10}, which represent contractions between double amplitudes or double and triple amplitudes:

$$x_1(a,b) = \frac{1}{2}\sum_{ij,c} a^{ac}_{ij}a^{bc}_{ij}, \quad \text{(A5)}$$

$$x_2(i,j) = \frac{1}{2}\sum_{k,ab} a^{ab}_{ik}a^{ab}_{jk}, \quad \text{(A6)}$$

$$x_3(ia,jb) = \sum_{kc} a^{ac}_{ik}a^{bc}_{jk}, \quad \text{(A7)}$$

$$x_4(ij,kl) = \frac{1}{2}\sum_{ab} a^{ab}_{ij}a^{ab}_{kl}, \quad \text{(A8)}$$

$$x_5(ab,cd) = \frac{1}{2}\sum_{ij} a^{ab}_{ij}a^{cd}_{ij}, \quad \text{(A9)}$$

$$x_6(l,f) = \frac{1}{4}\sum_{ij}\sum_{ab} a^{ab}_{ij}b^{abf}_{ijl}, \quad \text{(A10)}$$

$$x_7(i,kl,f) = \frac{1}{2}\sum_{j,ab} a^{ab}_{ij}b^{abf}_{kjl}, \quad \text{(A11)}$$

$$x_8(a,m,cd) = \frac{1}{2}\sum_{ij,b} a^{ab}_{ij}b^{cbd}_{ijm}, \quad \text{(A12)}$$

$$x_9(kl,f,ijm) = \frac{1}{2}\sum_{cd} a^{cd}_{kl}b^{cdf}_{ijm}, \quad \text{(A13)}$$

$$x_{10}(lc,im,af) = \sum_{kd} a^{cd}_{kl}b^{afd}_{ikm}. \quad \text{(A14)}$$

Intermediate arrays x_1–x_5 can be evaluated in $O(M^6)$ steps while x_6–x_8 and x_9–x_{10} require $O(M^7)$ and $O(M^8)$ steps, respectively.

DETERMINATION OF $E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$ [EQ. (27)]

Energy contributions $E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a$ are evaluated with the help of the new array $w_1(i,a)$ according to

$$E^{(6)}_{STQ}(\mathrm{II}) + E^{(6)}_{QTQ}(\mathrm{II})_a = \sum_{i,a} b^{a}_{i}w_1(i,a). \quad \text{(A15)}$$

Array $w_1(i,a)$ is constructed utilizing the definitions of arrays x_1–x_5, $z_5(i,bc,f)$, and $z_6(jk,ma)$ (see Table III):

$$\begin{aligned} w_1(i,a) &= \frac{1}{2}\sum_{bc,f} z_5(i,bc,f)\,x_5(bc,af) \\ &\quad - \sum_{cf} z_5(i,ac,f)\,x_1(c,f) \\ &\quad + \sum_{kc,f} z_5(k,ac,f)\,x_3(kc,if) \\ &\quad - \sum_{k,f} y_1(k,f)\,a^{af}_{ik} \\ &\quad + \frac{1}{2}\sum_{jk,m} z_6(jk,m,a)\,x_4(jk,im) \\ &\quad - \sum_{k,m} z_6(ik,m,a)\,x_2(k,m) \end{aligned}$$

$$+ \sum_{km,c} z_6(ik,m,c)x_3(kc,ma) - \sum_{m,c} y_2(m,c)a_{im}^{ac} \quad \text{(A16)}$$

where the additional arrays $y_1(k,f)$ and $y_2(m,c)$ are given by

$$y_1(k,f) = \frac{1}{2}\sum_{j,bc} a_{jk}^{bc} z_5(j,bc,f) \quad \text{(A17)}$$

and

$$y_2(m,c) = \frac{1}{2}\sum_{jk,b} a_{jk}^{bc} z_6(jk,m,b). \quad \text{(A18)}$$

Analysis of Eq. (A16) indicates that each term of $w_1(i,a)$ does not require more than $O(M^6)$ computational steps.

DETERMINATION OF $E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$ [EQ. (28)]

The energy terms $E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a$ are calculated according to

$$E_{DQQ}^{(6)}(\mathrm{II}) + E_{QQQ}^{(6)}(\mathrm{II})_a = \frac{1}{4}\sum_{ij}\sum_{ab} b_{ij}^{ab} w_2(ij,ab) \quad \text{(A19)}$$

in which the array $w_2(ij,ab)$ is defined by

$$\begin{aligned} w_2(ij,ab) &= -\sum_e \sum_P (-1)^P P(a/b) a_{ij}^{ae} y_3(b,e) \\ &+ \sum_m \sum_P (-1)^P P(i/j) a_{im}^{ab} y_4(j,m) \\ &+ \sum_{c,f} a_{ij}^{cf} y_5(ab,c,f) + \sum_{k,n} a_{kn}^{ab} y_6(ij,k,n) \\ &+ \sum_{k,e} \sum_P (-1)^P P(i/j) a_{ik}^{ae} y_7(jb,ke) \\ &+ \sum_{ef} \langle ab||ef\rangle y_8(ij,e,f) \\ &+ \sum_{mn} \langle mn||ij\rangle y_9(m,n,ab) \\ &- \sum_P (-1)^P (i/j|a/b) \\ &\times \left[\sum_{me} \langle ma||ie\rangle y_{10}(j,b,m,e) - \sum_{ke} a_{ik}^{ae} y_{11}(jb,ke) \right], \end{aligned} \quad \text{(A20)}$$

and the intermediate arrays y_3–y_{11} by Eqs. (A21)–(A29):

$$\begin{aligned} y_3(b,e) &= -\frac{1}{2}\sum_{kl,f} a_{kl}^{bf} x_{11}(kl,ef) \\ &+ \sum_{d,f} \langle bd||ef\rangle x_1(d,f) \\ &+ \sum_{ml,d} \langle md||le\rangle x_3(ld,mb) \\ &- \sum_{ml} \langle mb||le\rangle x_2(l,m), \end{aligned} \quad \text{(A21)}$$

$$\begin{aligned} y_4(j,m) &= -\frac{1}{2}\sum_{kl,n} \langle mn||kl\rangle x_4(kl,jn) \\ &+ \sum_{nl} \langle mn||jl\rangle x_2(l,n) \\ &+ \sum_{ld,e} \langle md||le\rangle x_3(ld,je) \\ &- \sum_{d,e} \langle md||je\rangle x_1(d,e), \end{aligned} \quad \text{(A22)}$$

$$\begin{aligned} y_5(ab,c,f) &= \sum_P (-1)^P P(a/b) \\ &\times \left[\sum_{d,e} \langle bd||ef\rangle x_5(cd,ae) + \sum_{ml} \langle mb||lf\rangle x_3(lc,ma) \right], \end{aligned} \quad \text{(A23)}$$

$$\begin{aligned} y_6(ij,k,n) &= \sum_P (-1)^P P(i/j) \\ &\times \left[\sum_{ml} \langle mn||jl\rangle x_4(kl,im) + \sum_{d,e} \langle nd||je\rangle x_3(kd,ie) \right] \\ &- \sum_{ce} a_{ij}^{ce} x_{13}(kc,ne), \end{aligned} \quad \text{(A24)}$$

$$y_7(jb,ke) = \sum_{l,f} a_{jl}^{bf} [x_{11}(kl,ef) + x_{12}(kl,ef)], \quad \text{(A25)}$$

$$y_8(ij,e,f) = \sum_c a_{ij}^{ce} x_1(c,f) + \sum_{k,c} a_{ik}^{ec} x_3(kc,jf), \quad \text{(A26)}$$

$$y_9(m,n,ab) = \sum_k a_{km}^{ab} x_2(k,n) + \sum_{k,c} a_{mk}^{ac} x_3(kc,nb), \tag{A27}$$

$$y_{10}(j,b,m,e) = \sum_{lc} a_{lm}^{bc} x_3(lc,je) + \sum_d a_{jm}^{db} x_1(d,e) - \sum_k a_{jk}^{be} x_2(k,m) + \frac{1}{2}\sum_{kl} a_{kl}^{be} x_4(kl,jm), \tag{A28}$$

$$\begin{aligned} y_{11}(j,b,m,e) = & \sum_{d,f} [\langle kd||jf\rangle x_5(ed,bf) \\ & - \langle bd||ef\rangle x_3(kd,jf)] \\ & - \sum_{n,l} [\langle kn||jl\rangle x_3(le,nb) \\ & - \langle nb||le\rangle x_4(kl,jn)] \\ & + \sum_{m,c} \left[a_{jm}^{bc} x_{13}(kc,me) + \langle kb\|mc\rangle x_3(me,jc) \right. \\ & \left. - \langle mc||je\rangle x_3(kc,mb) \right]. \end{aligned} \tag{A29}$$

The additional arrays $x_{11}(kl,ef)$, $x_{12}(mn,cd)$, and $x_{13}(kc,me)$ are due to contractions of double amplitudes a_{kl}^{cd} with two-electron integrals:

$$x_{11}(kl,ef) = \frac{1}{2}\sum_{cd} \langle cd||ef\rangle a_{kl}^{cd}, \tag{A30}$$

$$x_{12}(kl,ef) = \frac{1}{2}\sum_{mn} \langle kl||mn\rangle a_{mn}^{ef}, \tag{A31}$$

$$x_{13}(kc,me) = \sum_{l,d} \langle md||le\rangle a_{kl}^{cd}. \tag{A32}$$

All intermediate arrays contained in $w_2(ij,ab)$ do not require more than $O(M^6)$ computational steps.

DETERMINATION OF $E_{QHQ}^{(6)}$(II) [EQ. (36)]

If the term $E_{QHQ}^{(6)}$(II) is dissected into three parts, each part can be evaluated with the help of intermediate arrays x_1–x_5 in no more than $O(M^6)$ computational steps.

$$\begin{aligned} E_{QHQ}^{(6)}(\mathrm{II}) = & \sum_{mn}\sum_{ef} \langle mn||ef\rangle \\ & \times [\tfrac{1}{4} w_3(mn,ef)_a + w_3(mn,ef)_b \\ & + \tfrac{1}{4} w_3(mn,ef)_c]. \end{aligned} \tag{A33}$$

Arrays $w_3(mn,ef)_a$, $w_3(mn,ef)_b$, and $w_3(mn,ef)_c$ are determined by Eqs. (A34)–(A36):

$$w_3(mn,ef)_a = -\sum_{kl} a_{kl}^{ef} y_{16}(kl,mn) + \sum_{ab} x_5(ab,ef) y_{17}(ab,mn), \tag{A34}$$

$$w_3(mn,ef)_b = \sum_{lb} a_{ml}^{eb} y_{14}(nf,lb) + \sum_{jb} x_3(jb,me) y_{15}(nf,jb), \tag{A35}$$

$$w_3(mn,ef)_c = -\sum_{kl} x_4(kl,mn) y_{12}(kl,ef) + \sum_{ca} a_{mn}^{ca} y_{13}(ca,ef), \tag{A36}$$

where arrays y_{12}–y_{17} are given by

$$y_{12}(kl,ef) = \sum_b a_{kl}^{eb} x_1(b,f) - \sum_{jd} a_{lj}^{fd} x_3(ke,jd), \tag{A37}$$

$$y_{13}(ca,ef) = \sum_{ik} x_3(ia,ke) x_3(if,kc) - \sum_{bd} x_5(ab,fd) x_5(eb,cd) + x_1(a,f) x_1(c,e), \tag{A38}$$

$$\begin{aligned} y_{14}(nf,lb) = & -\sum_{kj} x_4(kl,jn) x_3(jb,kf) \\ & + x_2(l,n) x_1(b,f) \\ & - \sum_k x_3(lb,kf) x_2(k,n) \\ & + \sum_{kc} x_3(lc,kf) x_3(kb,nc) \\ & + \sum_{ac} x_5(ba,cf) x_3(lc,na), \end{aligned} \tag{A39}$$

$$y_{15}(nf,jb) = -\sum_{kc} a_{kj}^{cf} x_3(kc,nb) + \frac{1}{2}\sum_{kl} a_{kl}^{fb} x_4(kl,nj) - \sum_d a_{nj}^{db} x_1(d,f), \tag{A40}$$

$$y_{16}(kl,mn) = \sum_j x_4(kl,jn) x_2(j,m) - x_2(l,n) x_2(k,m) - \sum_{ij} x_4(li,mj) x_4(kj,ni)$$

$$- \sum_{bc} x_3(lb, mc)\, x_3(kc, nb), \tag{A41}$$

$$y_{17}(ab, mn) = \sum_{kc} a_{mk}^{ac}\, x_3(kc, nb). \tag{A42}$$

DETERMINATION OF $E_{TQD}^{(6)} + E_{TQQ}^{(6)}$(I) [EQ. (40)]

We refrain from using $u_9(ijkl, abcd)$ for the evaluation of $E_{TQD}^{(6)} + E_{TQQ}^{(6)}$(I) and rewrite Eq. (40):

$$\begin{aligned} E_{TQD}^{(6)} &+ E_{TQQ}^{(6)}(\mathrm{I}) \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)} \middle| \Phi_0 \right\rangle_C \\ &= \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(2)} \left(\overline{V} \hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle \\ &\quad + \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(1)} \left(\overline{V} \hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle. \end{aligned} \tag{A43}$$

In Eq. (A43), the first term can be obtained by

$$\begin{aligned} &\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \left(\overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &\qquad = \frac{1}{(3!)^2} \sum_{ijk} \sum_{abc} b_{ijk}^{abc} w_4(ijk, abc), \end{aligned} \tag{A44}$$

where array $w_4(ijk, abc)$ is defined by

$$\begin{aligned} &w_4(ijk, abc) \\ &\quad = \left\langle \Phi_{ijk}^{abc} \middle| \left[\overline{V} \hat{T}_2^{(1)} \hat{T}_2^{(2)} \right]_C \middle| \Phi_0 \right\rangle \qquad \text{(A45)} \\ &\quad = \sum_P (-1)^P P(i/jk|a/bc) \\ &\qquad \times \Bigg[\sum_f z_5(i, bc, f) b_{jk}^{af} \\ &\qquad + \sum_m z_6(jk, m, a) b_{im}^{bc} \\ &\qquad + \text{corresponding terms with double} \\ &\qquad\quad \text{amplitudes } a_d \text{ and } b_d \text{ interchanged} \Bigg] \end{aligned} \tag{A46}$$

Array $w_4(ijk, abc)$ resembles $u_{11}(ijk, abc)$ of Eq. (24) and, similar to u_{11}, can be evaluated in $O(M^7)$ steps.

The second term in Eq. (A43) can be combined with the matrix element

$$\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_1^{(2)} \left(\overline{V} \hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle$$

of the energy term $E_{TTS}^{(6)} + E_{TTQ}^{(6)}$(I) thus leading to a simpler form, in which the operator $\hat{T}_3^{(2)}$ does no longer occur.

$$\begin{aligned} &\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(2)} \left(\overline{V} \hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle \\ &+ \left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_1^{(2)} \left(\overline{V} \hat{T}_2^{(1)}\right)_C \middle| \Phi_0 \right\rangle \\ &\quad = \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^\dagger \left(\overline{V} \hat{T}_2^{(2)} \hat{T}_1^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &+ \left\langle \Phi_0 \middle| \left(\hat{T}_2^{(1)}\right)^\dagger \hat{T}_1^{(2)} \left(\overline{V} \hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \end{aligned} \tag{A47}$$

$$= \frac{1}{4} \sum_{ij} \sum_{ab} a_{ij}^{ab} [w_5(ij, ab) + 4 b_i^a u_2(j, b)]. \tag{A48}$$

This expression involves only $O(M^6)$ steps because $w_5(ij, ab)$ is equivalent to $u_{14}(ij, ab)$ when replacing the double amplitudes a_d by amplitudes b_d [see also Eq. (45)].

The last term in Eq. (A43) can be evaluated according to Eq. (A49):

$$\begin{aligned} &\left\langle \Phi_0 \middle| \left(\hat{T}_3^{(2)}\right)^\dagger \hat{T}_2^{(1)} \left(\overline{V} \hat{T}_2^{(2)}\right)_C \middle| \Phi_0 \right\rangle \\ &\qquad = \sum_{i,a} u_2(i, a) u_{16}(i, a), \end{aligned} \tag{A49}$$

which requires $O(M^7)$ steps.

DETERMINATION OF MATRIX ELEMENT $\langle \Phi_0 | \frac{1}{2} [(\hat{T}_2^{(1)})^\dagger]^2 \hat{T}_1^{(2)} (\overline{V} \hat{T}_2^{(1)})_C | \Phi_0 \rangle$ IN ENERGY TERM $E_{QTS}^{(6)} + E_{QTQ}^{(6)}$(I)

The matrix element

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

can be evaluated in terms of the intermediate array $u_{17}(l, d)$ [Eq. (59)]:

$$\begin{aligned} &u_{17}(l, d) \\ &\quad = \left\langle \Phi_0 \middle| \tfrac{1}{2} \left[\left(\hat{T}_2^{(1)}\right)^\dagger \right]^2 \left(\overline{V} \hat{T}_2^{(1)}\right)_C \middle| \Phi_l^d \right\rangle_C \\ &\quad = \sum_{k,c} a_{kl}^{cd} w_6(k, c) - \sum_{a,c,e} x_{18}(la, ec)\, x_4(cd, ae) \\ &\qquad - \sum_e x_{14}(l, e)\, x_1(e, d) \end{aligned}$$

$$+\sum_{i,k,e} x_{16}(il,ke)\,x_3(kd,ie)$$
$$+\sum_{k,b,e} x_{18}(kd,eb)\,x_3(lb,ke)$$
$$+\sum_{m,a,c} x_{17}(cd,ma)\,x_3(la,mc)$$
$$-\sum_{m} x_{15}(d,m)\,x_2(l,m)$$
$$-\sum_{m,i,j} x_{19}(jd,im)\,x_4(il,jm)$$
$$+\sum_{k,m,b} x_{19}(lb,km)\,x_3(kd,mb), \qquad \text{(A50)}$$

where $w_6(k,c)$ is defined by

$$w_6(k,c) = \sum_{jb,e} \langle je||bc\rangle x_3(jb,ke) - \sum_{b,e} \langle bc||ke\rangle x_1(b,e)$$
$$-\sum_{i,e} x_{14}(i,e)a_{ik}^{ce} - \frac{1}{2}\sum_{ab,e} \langle ab||ke\rangle x_5(ab,ce)$$
$$+\sum_{i,m,a} \langle ma||ik\rangle x_3(ia,mc)$$
$$-\sum_{i,m} \langle ik||mc\rangle x_2(i,m)$$
$$+\frac{1}{2}\sum_{ij,m} \langle ij||mc\rangle x_4(ij,mk)$$
$$-\sum_{m,b} x_{15}(b,m)a_{km}^{bc}. \qquad \text{(A51)}$$

Arrays x_{14}–x_{19} represent contractions of double amplitudes a_d with two-electron integrals as given in Eqs. (A52)–(A57):

$$x_{14}(l,e) = \frac{1}{2}\sum_{i,ab} a_{il}^{ab}\langle ie||ab\rangle, \qquad \text{(A52)}$$
$$x_{15}(d,m) = \frac{1}{2}\sum_{jk,c} a_{jk}^{cd}\langle jk||mc\rangle, \qquad \text{(A53)}$$
$$x_{16}(il,ke) = \frac{1}{2}\sum_{ab} a_{il}^{ab}\langle ke||ab\rangle, \qquad \text{(A54)}$$
$$x_{17}(cd,ma) = \frac{1}{2}\sum_{jk} a_{jk}^{cd}\langle jk||ma\rangle, \qquad \text{(A55)}$$
$$x_{18}(la,ec) = \sum_{i,b} a_{li}^{ab}\langle ie||bc\rangle, \qquad \text{(A56)}$$
$$x_{19}(jd,im) = \sum_{k,c} a_{kj}^{cd}\langle ik||mc\rangle. \qquad \text{(A57)}$$

None of the intermediate arrays in $u_{17}(l,d)$ involves more than $O(M^6)$ computational steps.

DETERMINATION OF $E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$ [EQ. (69)]

For simplicity, we split $E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})$ into the four parts of Eq. (A58):

$$E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II}) = \left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_a + \left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_b + \left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_c + \left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_d, \qquad \text{(A58)}$$

which differ in the contraction indices of products between double amplitudes a_d and two-electron integrals $\langle md||ef\rangle$ and $\langle mn||lf\rangle$: (a) $\sum_{me} a_{km}^{ce}\langle md||ef\rangle$ and $\sum_{nf} a_{kn}^{cf}\langle mn||lf\rangle$; (b) $\sum_{m} a_{im}^{ab}\langle md||ef\rangle$ and $\sum_{m} a_{im}^{ab}\langle mn||lf\rangle$); (c) $\sum_{f} a_{ij}^{af}\langle md||ef\rangle$ and $\sum_{f} a_{ij}^{af}\langle mn||lf\rangle$) as well as (d) $\sum_{mn} a_{mn}^{cd}\langle mn||lf\rangle$ and $\sum_{ef} a_{ij}^{ef}\langle md||ef\rangle$. The four parts are given by Eqs. (A59)–(A62):

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_a = \frac{1}{32}\sum_{ij,ab}\sum_{kl,cd} a_{ij}^{ab}a_{kl}^{cd}\Bigg\{\sum_{P}(-1)^P P(ab/cd|k/ijl)$$
$$\times\sum_{f}\sum_{P'}(-1)^{P'}P'(c/d)\sum_{me}\langle md||ef\rangle a_{km}^{ce}b_{ijl}^{abf}$$
$$-\sum_{P}(-1)^P P(c/abd|ij/kl)\sum_{m}\sum_{P'}(-1)^{P'}$$
$$\times P'(k/l)\sum_{nf}\langle mn||lf\rangle a_{kn}^{cf}b_{ijm}^{abd}\Bigg\}$$
$$= \frac{1}{4}\sum_{ij,ab}\sum_{kl,cd} a_{ij}^{ab}a_{kl}^{cd}\Bigg\{\sum_{m,ef}\langle md||ef\rangle$$
$$\times\left(a_{km}^{ce}b_{ijl}^{abf} + 2a_{im}^{ae}b_{klj}^{cfb} - a_{im}^{ce}b_{kjl}^{abf} - 2a_{lm}^{ae}b_{ijk}^{fbc}\right)$$
$$-\sum_{mn,f}\langle mn||lf\rangle\left(a_{kn}^{cf}b_{ijm}^{abd} + 2a_{in}^{af}b_{kmj}^{cdb}\right.$$
$$\left.-2a_{in}^{cf}b_{kjm}^{abd} - a_{kn}^{af}b_{ijm}^{cbd}\right)\Bigg\}, \qquad \text{(A59)}$$

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_b = -\frac{1}{32}\sum_{ij,ab}\sum_{kl,cd} a_{ij}^{ab}a_{kl}^{cd}\sum_{P}(-1)^P P(ab/cd|i/jkl)$$
$$\times\sum_{m}\Bigg(\frac{1}{2}\sum_{ef}\sum_{P'}(-1)^{P'}P'(c/d)\langle md||ef\rangle b_{jkl}^{ecf}$$

$$+\sum_{P'}(-1)^{P'}P'(l/jk)\sum_{nf}\langle mn||lf\rangle b_{jkn}^{fcd}\Big)a_{im}^{ab}$$

$$=\frac{1}{4}\sum_{ij,ab}\sum_{kl,cd}a_{ij}^{ab}a_{kl}^{cd}\Big\{\sum_{m,ef}\langle md||ef\rangle\big(-a_{im}^{ab}b_{jkl}^{ecf}$$

$$-2a_{km}^{cb}b_{ijl}^{aef}+a_{km}^{ab}b_{ijl}^{cef}+2a_{im}^{cb}b_{jkl}^{eaf}\big)$$

$$-\sum_{mn,f}\langle mn||lf\rangle\big(a_{im}^{ab}b_{jkn}^{fcd}+2a_{km}^{cb}b_{ijn}^{afd}$$

$$+\tfrac{1}{2}a_{km}^{cd}b_{ijn}^{abf}-a_{im}^{cd}b_{kjn}^{abf}$$

$$-\tfrac{1}{2}a_{km}^{ab}b_{ijn}^{cfd}+4a_{mj}^{cb}b_{ikn}^{afd}\big)\Big\}, \tag{A60}$$

$$\big[E_{QPT}^{(6)}(\mathrm{II})+E_{QPQ}^{(6)}(\mathrm{II})\big]_c$$

$$=\frac{1}{32}\sum_{ij,ab}\sum_{kl,cd}a_{ij}^{ab}a_{kl}^{cd}\sum_{P}(-1)^{P}P(a/bcd|ij/kl)$$

$$\times\sum_{f}\Big(\sum_{P'}(-1)^{P'}P'(d/bc)\sum_{me}\langle md||ef\rangle b_{klm}^{bce}$$

$$+\frac{1}{2}\sum_{mn}\sum_{P'}(-1)^{P'}P'(k/l)\langle mn||lf\rangle b_{kmn}^{cdb}\Big)a_{ij}^{af}$$

$$=\frac{1}{4}\sum_{ij,ab}\sum_{kl,cd}a_{ij}^{ab}a_{kl}^{cd}\Big\{\langle md||ef\rangle\big(a_{ij}^{af}b_{klm}^{bce}$$

$$+\tfrac{1}{2}a_{ij}^{cf}b_{klm}^{abe}-a_{kl}^{af}b_{ijm}^{cbe}-2a_{ki}^{cf}b_{ljm}^{abe}$$

$$+\tfrac{1}{2}a_{kl}^{cf}b_{ijm}^{abe}+4a_{il}^{af}b_{jkm}^{bce}\big)$$

$$+\sum_{mn,f}\langle mn||lf\rangle\Big[\tfrac{1}{2}\big(a_{ij}^{af}b_{kmn}^{cdb}-a_{ij}^{cf}b_{kmn}^{adb}\big)$$

$$+a_{kj}^{cf}b_{inm}^{abd}+a_{ik}^{af}b_{jmn}^{bdc}\Big]\Big\}, \tag{A61}$$

$$\big[E_{QPT}^{(6)}(\mathrm{II})+E_{QPQ}^{(6)}(\mathrm{II})\big]_d$$

$$=-\frac{1}{32}\sum_{ij,ab}\sum_{kl,cd}a_{ij}^{ab}a_{kl}^{cd}$$

$$\times\Big\{\sum_{P}(-1)^{P}P(ab/cd|l/ijk)$$

$$\times\sum_{mn}\langle mn||lf\rangle a_{mn}^{cd}b_{ijk}^{abf}$$

$$+\sum_{P}(-1)^{P}P(d/abc|ij/kl)$$

$$\times\sum_{ef}\langle md||ef\rangle a_{ij}^{ef}b_{klm}^{cab}\Big\}$$

$$=-\frac{1}{16}\sum_{ij,ab}\sum_{kl,cd}a_{ij}^{ab}a_{kl}^{cd}\Big\{\sum_{mn,f}\langle mn||lf\rangle$$

$$\times\big(a_{mn}^{cd}b_{ijk}^{abf}+a_{mn}^{ab}b_{ijk}^{cdf}+2a_{mn}^{ac}b_{ijk}^{dbf}\big)$$

$$+\sum_{m,ef}\langle md||ef\rangle\big(a_{ij}^{ef}b_{klm}^{cab}+a_{kl}^{ef}b_{ijm}^{abc}-2a_{il}^{ef}b_{kjm}^{abc}\big)\Big\}. \tag{A62}$$

In order to evaluate these parts in no more than $O(M^8)$ computational steps, we need to define the additional intermediate arrays w_7–w_{18} in terms of arrays x_1–x_{10}:

$$w_7(md,ef)=\sum_{l}x_3(ld,me)\,x_6(l,f)$$

$$+\sum_{j,b}x_3(jb,me)\,x_8(d,j,fb), \tag{A63}$$

$$w_8(mn,lf)=\sum_{d}x_3(ld,nf)\,x_6(m,d)$$

$$+\sum_{j,b}x_3(jb,nf)\,x_7(l,jm,b), \tag{A64}$$

$$w_9(ic,df)=\frac{1}{2}\sum_{kl}a_{kl}^{cd}x_7(i,kl,f)$$

$$-\sum_{k,a}a_{ik}^{ad}x_8(c,k,fa), \tag{A65}$$

$$w_{10}(ic,ml)=\sum_{k,d}a_{kl}^{cd}x_7(ik,md)$$

$$+\frac{1}{2}\sum_{ad}x_8(c,m,ad)a_{il}^{ad}, \tag{A66}$$

$$w_{11}(md,ef)=\sum_{j}x_2(j,m)\,x_8(d,j,ef)$$

$$-\sum_{l,b}x_3(ld,mb)\,x_8(b,l,ef), \tag{A67}$$

$$w_{12}(m,n,l,f)$$

$$=\sum_{j}x_2(j,n)\,x_7(l,mj,f)$$

$$+\sum_{bd}x_3(ld,nb)\,x_8(b,m,fd)$$

$$+x_2(l,n)\,x_6(m,f)$$

$$-\sum_{ik}x_4(kl,in)\,x_7(i,km,f)$$

$$+\frac{1}{2}\sum_{ij,k}x_4(ij,kn)\,x_9(kl,f,ijm)$$

$$+\sum_{i,ac}x_3(ia,nc)\,x_{10}(lc,im,af), \tag{A68}$$

$$w_{13}(k,l,c,d) = \frac{1}{2}\sum_{ij,m} x_4(ij,km)\,x_{20}(md,c,ijl) - \sum_{ja,m} x_3(ja,mc)\,x_{20}(md,a,jkl), \quad \text{(A69)}$$

$$w_{14}(md,ef) = -\sum_b x_1(b,f)\,x_8(d,m,be) - \sum_{a,c} x_5(cd,af)\,x_8(a,m,ce) - \sum_{i,l} x_3(ld,if)\,x_7(i,lm,e) + x_1(d,f)\,x_6(m,e) + \sum_{kl,c} a_{kl}^{cd}\,x_{21}(cf,e,klm) + \sum_{jb,l} x_3(jb,lf)\,x_{10}(ld,jm,be), \quad \text{(A70)}$$

$$w_{15}(mn,lf) = \sum_b x_1(b,f)\,x_7(l,mn,b) - \sum_{j,d} x_3(ld,jf)\,x_7(j,mn,d) + \frac{1}{2}\sum_{kl,d} a_{kl}^{cd}\,x_{21}(cf,d,kmn) - \sum_{j,k,b} x_3(jb,kf)\,x_9(kl,b,jmn), \quad \text{(A71)}$$

$$w_{16}(mn,lf) = \sum_k x_4(mn,kl)\,x_6(k,f) + \frac{1}{2}\sum_{ij} x_4(ij,mn)\,x_7(l,ij,f), \quad \text{(A72)}$$

$$w_{17}(md,ef) = \frac{1}{2}\sum_{ab} x_5(ef,ab)\,x_8(d,m,ab) + \sum_c x_5(cd,ef)\,x_6(m,c), \quad \text{(A73)}$$

$$w_{18}(k,l,c,d) = -\sum_{a,f} x_{17}(ac,lf)\,x_8(a,k,df) + \sum_{i,m} x_{16}(il,md)\,x_7(i,km,c), \quad \text{(A74)}$$

with

$$x_{20}(md,c,ijl) = \frac{1}{2}\sum_{ef} \langle md||ef\rangle b_{ijl}^{cef}, \quad \text{(A75)}$$

$$x_{21}(cf,e,klm) = \frac{1}{2}\sum_{ab} x_5(ab,cf)\,b_{klm}^{abe}. \quad \text{(A76)}$$

Equations (A59)–(A62) can be rewritten in the following way:

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_a = \sum_{md}\sum_{ef}\langle md||ef\rangle w_7(md,ef) - \sum_{mn}\sum_{lf}\langle mn||lf\rangle w_8(mn,lf) - \sum_{i,c}\sum_{df} x_{18}(ic,df)\,w_9(ic,df) + \sum_{mn}\sum_{i,c} x_{19}(ic,ml)\,w_{10}(ic,ml), \quad \text{(A77)}$$

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_b = \frac{1}{2}\sum_{md}\sum_{ef}\langle md||ef\rangle w_{11}(md,ef) + \sum_{mn}\sum_{lf}\langle mn||lf\rangle w_{12}(m,n,l,f) + \sum_{kl,cd} a_{kl}^{cd}\,w_{13}(k,l,c,d), \quad \text{(A78)}$$

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_c = \sum_{md}\sum_{ef}\langle md||ef\rangle w_{14}(md,ef) + \frac{1}{2}\sum_{mn}\sum_{lf}\langle mn||lf\rangle w_{15}(mn,lf), \quad \text{(A79)}$$

$$\left[E_{QPT}^{(6)}(\mathrm{II}) + E_{QPQ}^{(6)}(\mathrm{II})\right]_d = -\frac{1}{2}\left[\sum_{mn}\sum_{lf}\langle mn||lf\rangle w_{16}(mn,lf) + \sum_{md}\sum_{ef}\langle md||ef\rangle w_{17}(md,ef)\right] + \sum_{kl,cd} a_{kl}^{cd}\,w_{18}(k,l,c,d). \quad \text{(A80)}$$

Analysis of arrays w_7–w_{18} reveals that computationally the most demanding steps are the determination of w_{12}–w_{15}, which depend on x_9, x_{10}, x_{20}, and x_{21}, respectively, and accordingly, involve $O(M^8)$ steps. All other intermediate arrays do not require more than $O(M^7)$ steps.

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