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Editorial

Explicit- r_{12} correlation methods and local correlation methods

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Equations of explicitly-correlated coupled-cluster methods†

Toru Shiozaki,^{ac} Muneaki Kamiya,^a So Hirata^{*a} and Edward F. Valeev^b

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The tensor contraction expressions defining a variety of high-rank coupled-cluster energies and wave functions that include the interelectronic distances (r_{12}) explicitly (CC-R12) have been derived with the aid of a newly-developed computerized symbolic algebra SMITH. Efficient computational sequences to perform these tensor contractions have also been suggested, defining intermediate tensors—some reusable—as a sum of binary tensor contractions. SMITH can elucidate the index permutation symmetry of intermediate tensors that arise from a Slater-determinant expectation value of any number of excitation, deexcitation and other general second-quantized operators. SMITH also automates additional algebraic transformation steps specific to R12 methods, *i.e.* the identification and isolation of the special intermediates that need to be evaluated analytically and the resolution-of-the-identity insertion to facilitate high-dimensional molecular integral computation. The tensor contraction expressions defining the CC-R12 methods including through the connected quadruple excitation operator (CCSDTQ-R12) have been documented and efficient computational sequences have been suggested not just for the ground state but also for excited states *via* the equation-of-motion formalism (EOM-CC-R12) and for the so-called Λ equation (Λ -CC-R12) of the CC analytical gradient theory. Additional equations (the geminal amplitude equation) arise in CC-R12 that need to be solved to determine the coefficients multiplying the r_{12} -dependent factors. The operation cost of solving the geminal amplitude equations of rank- k CC-R12 and EOM-CC-R12 (right-hand side) scales as $O(n^6)$ ($k = 2$) or $O(n^7)$ ($k \geq 3$) with the number of orbitals n and is surpassed by the cost of solving the usual amplitude equations $O(n^{2k+2})$. While the complexity of the geminal amplitude equations of Λ - and EOM-CC-R12 (left-hand side) nominally scales as $O(n^{2k+2})$, it is less than that of the other $O(n^{2k+2})$ terms in the usual amplitude equations. This suggests that the unabridged equations should be solved in high-rank CC-R12 for benchmark accuracy.

I. Introduction

The explicit inclusion of the interelectronic (r_{12}) degrees of freedom in electron wave functions^{1,2} significantly reduces the errors in the wave functions and energies arising from the incompleteness of the one-electron basis set (see ref. 3 and 4 and references therein). The Slater-type correlation factor first proposed by Ten-no⁵ allows one to recover typically 96% of the complete-basis-set second-order Møller–Plesset (MP2) correlation energies with the aug-cc-pVDZ basis set and 99% with the aug-cc-pVTZ basis set;^{4,6,7} these figures are considerably greater than those of the standard MP2 method (~ 70 and 90%). In these MP2-R12 calculations, the majority of the residual errors is ascribed to the higher-order electron correlation effects rather than to the basis-set incompleteness

and it is hence important to address such effects with high-rank electron-correlation treatments such as the coupled-cluster (CC) methods.

Noga *et al.* were among the first to study the CC methods including r_{12} -dependent terms (CC-R12)^{8–12} within the so-called standard approximation (SA).¹³ This approximation amounted to evaluating high-dimensional molecular integrals with the aid of the resolution-of-the-identity (RI) insertion using the same basis functions that expanded the Hartree–Fock orbitals. SA dramatically simplified the CC-R12 equations, but was effective only for large orbital basis sets.¹³ This problem was remedied by Klopper and Samson, who introduced a separate (and large) auxiliary basis set (ABS) for the RI.¹⁴ The numerical shortcomings of the ABS approach were rectified by Valeev, who proposed a more robust way to utilize an ABS and called it the complementary auxiliary basis set (CABS) method.^{15,16} Ten-no explored the use of a multicenter quadrature as a variant of ABS.¹⁷ These advances allowed the orbital basis set (OBS) to be kept relatively small and the accuracy of the RI approximation to be varied independently. These approaches, however, resulted in the CC-R12 formalisms that are much more complex than those based on the SA. Hence, several groups explored approximate formalisms utilizing the CABS. First, Fliegel *et al.* introduced an approximate CC-R12 with the connected

^a Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611-8435, USA.
E-mail: hirata@qtp.ufl.edu

^b Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061-0002, USA

^c Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo, 113-8656, Japan

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single and double excitation operators (CCSD-R12) termed CCSD(R12).^{18–20} Furthermore, CC-R12 was extended to excited states by Fliegl *et al.* in the CC2 approximation.^{21,22} Recently, Adler *et al.* proposed a further simplification of CCSD-R12 and CCSD(R12).²³ Independently, Valeev suggested introducing the r_{12} -dependent terms by the Löwdin perturbation theory using the CCSD wave function as a reference; the simplest of such methods, CCSD(2)_{R12}, had an accuracy comparable to that of the iterative CCSD(R12) method and could be implemented more easily.²⁴ It may be said that optimal algorithmic details and standard implementation practices of efficient and accurate CC-R12 methods are being established.

Nonetheless, unabridged implementations of CCSD-R12 and its higher-rank analogues, their excited-state counterparts *via* the equation-of-motion (EOM) formalism, and their analytical gradient capabilities based on the Λ equations have not appeared. The CCSD-R12 method adds the so-called geminal amplitude equation determining the amplitudes of the r_{12} -dependent terms to those that correspond to the usual CC energy and amplitude equations. As we show in this work, the size dependence of the operation cost of solving the geminal amplitude equation is the same as that of ordinary T amplitude equations in CCSD [$O(n^6)$ with n being the number of orbitals] but with a much greater prefactor, offering an incentive to neglect or approximate r_{12} -dependent terms in the former. However, this incentive vanishes for higher-rank CC-R12 methods because the operation cost of the amplitude equations increases exponentially with the excitation rank while that of the geminal amplitude equation remains $O(n^7)$ for CCSDT-R12 and higher. In this sense, it is meaningful to document and analyze the complete set of the equations that define high-rank CC-R12 and related methods. A pioneering study of the equations of CC-R12 including through the connected triple excitation operator (CCSDT-R12) was reported by Noga and Kutzelnigg.⁹

The formula derivation and computer implementation of high-rank CC-R12 methods involve complex symbolic manipulation processes which, in practice, can no longer be performed reliably by hand. This is already the case with the high-rank members of the conventional CC and EOM-CC methods, the derivation and implementation of which are computerized today. Kállay and Surján invented the string-based algorithm, which enumerated and evaluated diagrammatic contributions to the CC and EOM-CC equations at any given rank on the fly.^{25,26} Hirata developed the symbolic algebra code TCE,^{27–29} which automated the formula derivation and implementation processes of the CC, EOM-CC and related methods. Beginning with the definition of a method as a set of few physical equations (*ansatz*) written in terms of expectation values of second-quantized operators in a Slater determinant, TCE derives the corresponding tensor contraction equations by applying Wick's theorem (*derivation*). It then transforms the equations into efficient computational sequences exposing compact data layout and reuse, introducing the intermediate tensors ("intermediates") as a sum of binary tensor contractions (*transformation*). It eventually translates the computational sequences into parallel-executable codes that take advantage of spin symmetry (in the spin-orbital formalisms),

real Abelian point-group symmetry and index permutation symmetry (*implementation*).

Among these steps, the exploitation of index permutation symmetry is especially important not just for keeping the operation and memory costs manageable but also for ensuring Fermi–Dirac statistics of electronic wave functions. Unlike the physical tensors (*e.g.* molecular integrals, excitation amplitudes), which are antisymmetric with respect to an interchange of any pair of covariant or contravariant indices, the intermediates and their index permutation symmetry are not necessarily known *a priori*. What makes the algorithms of Kállay and Surján and those of Hirata feasible is the key observation²⁵ that, for a certain class of electron-correlation methods, intermediates can be made to have known index permutation symmetry by restricting permissible computational sequences. For instance, in the CC method of any rank, the intermediates have two covariant and two contravariant groups of permutable indices when binary contractions of excitation amplitudes are barred.

Owing to the presence of new physical tensors containing an r_{12} -dependent factor, the CC-R12 methods do not belong to the class of methods that can be handled by the aforementioned computerized symbolic algebra. To accommodate them, it is necessary to elucidate the index permutation symmetry of the intermediates that can arise from a wider class of electron-correlation methods and less restricted computational sequences. Furthermore, an implementation of the CC-R12 methods involves three additional algebraic transformation steps that are time-consuming and error-prone when performed manually. First, some special intermediates must be identified and isolated to ensure the analytical elimination of the $1/r_{12}$ Coulomb singularity in the Hamiltonian with the r_{12} -dependent factor. Second, the RI must be introduced judiciously to reduce effectively the rank of the resulting high-dimensional molecular integrals and facilitate their rapid evaluation. Third, certain recurring intermediates must be precalculated, stored and reused. These symbol manipulation steps are tedious but highly systematic and ideally carried out by a computer.

The objective of this paper is twofold. The first objective is to describe the new symbolic algebra code SMITH (ref. 30) that automates the *derivation* and *transformation* processes of a much wider class of electron-correlation methods, including the CC-R12 methods, than could be handled previously. To achieve this goal, SMITH can elucidate the index permutation symmetry of intermediates arising from unrestricted computational sequences of the methods that are defined by Slater-determinant expectation values of a product of any number of excitation, deexcitation and other more general operators. SMITH can also perform the additional algebraic transformation steps unique to the R12 methods.

The second objective is to apply SMITH to the high-rank CC-R12 *ansätze* and document the resulting tensor contraction equations and computational sequences that define the intermediates, adopting the state-of-the-art R12 methodology (modified *ansatz* 2 and the CABS of Valeev). The CC-R12 methods including up to the connected quadruple excitation operator (CCSD-R12, CCSDT-R12 and CCSDTQ-R12) are analyzed. Furthermore, we extend the CC-R12 methods to

excited states *via* the EOM formalism^{31–36} and to the related Λ equations in the CC analytical gradient theory.³⁷ The corresponding tensor contraction equations are derived and computational sequences (intermediates) are suggested for up to EOM- and Λ -CCSDTQ-R12.

II. CC-R12 equations

A CCSD-R12 theory

We begin with a brief overview of the ansatz of the CC-R12 methods⁹ in the spin-orbital formalism using CCSD-R12 as an example. Its wave function for the electronic ground state is parametrized as

$$|\Psi\rangle = \exp(\hat{S})|\Phi_0\rangle, \quad (1)$$

where $|\Phi_0\rangle$ is a single-determinant [typically, but not limited to, Hartree-Fock (HF)] reference wave function and

$$\hat{S} = \hat{T} + \hat{\mathcal{F}}. \quad (2)$$

In the above, \hat{T} is the usual cluster excitation operator, *i.e.*

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad (3)$$

with

$$\hat{T}_1 = t_i^a \{a^\dagger i\}, \quad (4)$$

$$\hat{T}_2 = \frac{1}{4} t_{ij}^{ab} \{a^\dagger b^\dagger ji\}, \quad (5)$$

where a, b, c, d and a_n denote particle indices (virtual orbitals) in the space spanned by the orbital basis set; i, j, k, l, m and i_n hole indices (occupied orbital) in the same space; and p, q, r, s either (see Table 1). Henceforth repeated indices in an equation imply the summation over them with no restrictions to the index domain arising from the index permutation symmetry of tensors and $\{\dots\}$ brings the operators in the normal order.

The new operator $\hat{\mathcal{F}}$, which commutes with \hat{T} , is a product of molecular integrals $F_{kl}^{\alpha\beta}$ involving an explicit r_{12} -dependent factor (correlation factor) and geminal amplitudes t_{ij}^{kl} and is written as⁹

$$\hat{\mathcal{F}} = [\hat{F}\hat{t}]_C = \frac{1}{8} F_{kl}^{\alpha\beta} t_{ij}^{kl} \{\alpha^\dagger \beta^\dagger ji\}, \quad (6)$$

with

$$\hat{F} = \frac{1}{4} F_{kl}^{\alpha\beta} \{\alpha^\dagger \beta^\dagger lk\}, \quad (7)$$

$$\hat{t} = \frac{1}{4} t_{ij}^{kl} \{k^\dagger l^\dagger ji\}. \quad (8)$$

It is stipulated that F and t are antisymmetric with respect to the interchanges of contravariant (covariant) indices.

In the second equality in eqn (6), F and t are required to be diagrammatically connected through two hole lines (as indicated by “[\dots]_C”). The Greek symbols ($\alpha, \beta, \gamma, \delta, \alpha_n$) label particle indices (virtual orbitals) in the hypothetical complete basis set, which will be obliterated in the computational sequences that are subject to implementation (*vide infra*). It is assumed for convenience that the virtual orbitals in the orbital basis set ($\{\phi_a\}$) represent a subset of those in the complete basis set ($\{\phi_\alpha\}$) and hence either $\hat{P}_n \phi_\alpha(r_n) = 0$ or $\hat{P}_n \phi_\alpha(r_n) = \phi_\alpha(r_n)$ must hold, where \hat{P}_n is the projector onto the space spanned by $\{\phi_p(r_n)\}$.

Because $\hat{\mathcal{F}}$ is responsible for capturing just the two-electron correlation effects, it should satisfy

$$\hat{\mathcal{F}} = \hat{Q}_{12} \hat{\mathcal{F}}, \quad (9)$$

where \hat{Q}_{12} is the strong-orthogonality projection operator defined by

$$\hat{Q}_{12} \phi_i(r_1) = 0, \quad (10a)$$

$$\hat{Q}_{12} \phi_i(r_2) = 0, \quad (10b)$$

for any i . One such definition of \hat{Q}_{12} is expressed as^{14,38}

$$\hat{Q}_{12}^{(1)} = (1 - \hat{P}_1)(1 - \hat{P}_2), \quad (11)$$

which is known as “ansatz 1” of Kutzelnigg and Klopper.¹³ An alternative definition of \hat{Q}_{12} (“ansatz 2”) is

$$\hat{Q}_{12}^{(2)} = (1 - \hat{O}_1)(1 - \hat{O}_2), \quad (12)$$

where \hat{O}_n is the projector onto the space spanned by $\{\phi_i(r_n)\}$.³⁹ This ansatz is often preferred as it leads to smaller basis set errors when used in MP2-R12. It is also desirable for the geminal pairs produced by $\hat{\mathcal{F}}$ to be orthogonal to $\phi_a(r_1)\phi_b(r_2)$ products to avoid double counting the correlation energies that are already accounted for by the conventional correlation methods. This is achieved by “modified ansatz 2” introduced by Valeev¹⁵ in the form

$$\hat{Q}_{12}^{(2)} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2 \quad (13a)$$

$$= 1 - \hat{P}_1 \hat{P}_2 - \hat{O}_1(1 - \hat{P}_2) - (1 - \hat{P}_1)\hat{O}_2 \quad (13b)$$

$$= \hat{V}_1(1 - \hat{P}_2) + (1 - \hat{P}_1)\hat{V}_2 + (1 - \hat{P}_1)(1 - \hat{P}_2), \quad (13c)$$

where \hat{V}_n is the projector onto the space spanned by $\{\phi_a(r_1)\}$ (*i.e.* $\hat{P}_n = \hat{O}_n + \hat{V}_n$). Note that this ansatz was implicitly suggested in ref. 13 and sometimes referred to as “ansatz 3”.⁷

Adopting the projector of eqn (13a)–(13c) leads to the following definition for the molecular integrals $F_{kl}^{\alpha\beta}$:

Table 1 Sets and indices of spin orbitals and corresponding projectors

Set	Index	Projector	Spin orbital
$\{\phi_p\}$	p, q, r, s	\hat{P}	Spin orbitals in the orbital basis
$\{\phi_i\}$	i, j, k, l, m, i_n	\hat{O}	Occupied orbitals in the orbital basis
$\{\phi_a\}$	a, b, c, d, a_n	\hat{V}	Virtual orbitals in the orbital basis
$\{\phi_\kappa\}$	$\kappa, \lambda, \mu, \nu$	1	Spin orbitals in the complete basis
$\{\phi_\alpha\}$	$\alpha, \beta, \gamma, \delta, \alpha_n$	$1 - \hat{O}$	Virtual orbitals in the complete basis
$\{\phi_{\alpha'}\}$	α', α'_n	$1 - \hat{P}$	Virtual orbitals in the complete basis that do not belong to $\{\phi_a\}$
$\{\phi_{a'}\}$	a', b', a'_n	\hat{P}'	Virtual orbitals in the CABS

$$F_{kl}^{\alpha\beta} = \begin{cases} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\alpha(\mathbf{r}_1)^* \phi_\beta(\mathbf{r}_2)^* F_{12} \{ \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2) - \phi_l(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \}, & \text{if } \hat{P}_1 \phi_\alpha = 0 \text{ or } \hat{P}_2 \phi_\beta = 0; \\ 0, & \text{otherwise } (\hat{P}_1 \phi_\alpha = \phi_\alpha \text{ and } \hat{P}_2 \phi_\beta = \phi_\beta). \end{cases} \quad (14)$$

Various forms of the explicitly r_{12} -dependent factor (the correlation factor) can be inserted in eqn (14), e.g. the Slater-type function of r_{12} ,⁵

$$F_{12} = \exp(-\gamma r_{12}), \quad (15)$$

where γ is a positive constant. Other choices include the linear r_{12} function,^{2,13,38} Gaussian-type function^{40–43} and Gaussian-damped linear r_{12} function.⁴⁴

The unknown parameters in the wave function, *i.e.* the T amplitudes in eqn (4) and (5), the geminal t amplitudes in eqn (6) and correlation energy E_0 are determined by solving the equations obtained by substituting the wave function [eqn (1)] into the Schrödinger equation and projecting it onto the determinants accessible by the action of \hat{S} on $|\Phi_0\rangle$. This leads to what correspond to the energy and T_1 and T_2 amplitude equations of CCSD:⁹

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E_0, \quad (16)$$

$$\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0, \quad (17)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0, \quad (18)$$

where Φ_i^a and Φ_{ij}^{ab} are singly and doubly excited determinants from Φ_0 respectively, and a new equation:

$$\langle \Phi_{ij}^{kl} | \bar{H} | \Phi_0 \rangle = 0. \quad (19)$$

This last equation (the geminal amplitude equation) is obtained by projecting the Schrödinger equation onto the geminal replacements

$$|\Phi_{ij}^{kl}\rangle = [\hat{F}\{k^\dagger l^\dagger ji\}]_C |\Phi_0\rangle, \quad (20)$$

in which we imposed the connectedness in the same meaning as in eqn (6). Note that the number of individual equations in eqn (19) is identical to the number of the geminal t amplitudes (n_h^4 with n_h being the number of occupied orbitals). \bar{H} is the CCSD-R12 similarity-transformed Hamiltonian defined with the usual normal-ordered Hamiltonian \hat{H}_N by

$$\bar{H} = \exp(-\hat{S}) \hat{H}_N \exp(\hat{S}) = [\hat{H}_N \exp(\hat{S})]_C, \quad (21)$$

$$\hat{H}_N = f_{\lambda}^{\kappa} \{ \kappa^\dagger \lambda \} + \frac{1}{4} v_{\mu\nu}^{\kappa\lambda} \{ \kappa^\dagger \lambda^\dagger \nu \mu \}, \quad (22)$$

where f and v are Fock and antisymmetrized two-electron integral matrices respectively, and \hat{H}_N and \hat{S} must be diagrammatically connected in the right-hand side of eqn (21). The Greek symbols ($\kappa, \lambda, \mu, \nu$) in eqn (22) refer to the spin orbitals from a complete (and thus infinite) set obtained as a union of $\{\phi_i\}$ and $\{\phi_\alpha\}$.

We must now address how the sums over the complete basis set indices are eliminated to yield computationally tractable equations. The following tensor contractions (“special intermediates” shown in diagrammatic form in Fig. 1) involve certain two-electron integrals that must be evaluated before RI insertions to ensure the *analytical* cancellation between the $1/r_{12}$ singularity and the r_{12} -dependent factor:

$$V_{ij}^{pq} = \frac{1}{2} v_{\alpha\beta}^{pq} F_{ij}^{\alpha\beta}, \quad (23)$$

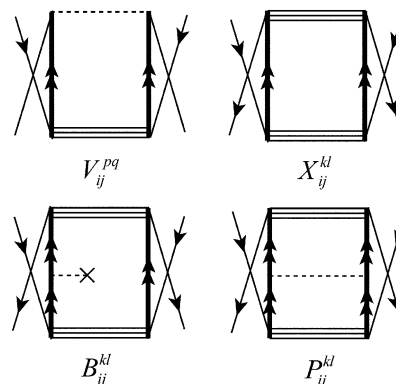


Fig. 1 Special intermediates that are evaluated as a whole (not as a tensor contraction) by individual molecular integral subroutines. The bold lines with double arrow stand for particles in a complete basis set, the triple vertices denote F and the dotted vertices f or v .⁹

$$X_{ij}^{kl} = \frac{1}{2} F_{\alpha\beta}^{kl*} F_{ij}^{\alpha\beta}, \quad (24)$$

$$B_{ij}^{kl} = F_{\alpha\beta}^{kl*} f_{\gamma}^{\alpha} F_{ij}^{\beta\gamma}, \quad (25)$$

$$P_{ij}^{kl} = \frac{1}{4} F_{\alpha\beta}^{kl*} v_{\gamma\delta}^{\alpha\beta} F_{ij}^{\gamma\delta}. \quad (26)$$

For example, using the projector in eqn (13b) allows one to rewrite eqn (23) as

$$\begin{aligned} V_{ij}^{pq} &= \frac{1}{2} v_{\kappa\lambda}^{pq} F_{ij}^{\kappa\lambda} - \frac{1}{2} v_{rs}^{pq} F_{ij}^{rs} - v_{m\alpha}^{pq} F_{ij}^{m\alpha'} \\ &= (F_{12}/r_{12})_{ij}^{pq} - \frac{1}{2} v_{rs}^{pq} F_{ij}^{rs} - v_{m\alpha}^{pq} F_{ij}^{m\alpha'}, \end{aligned} \quad (27)$$

where α' denotes an index from another infinite basis set $\{\phi_{\alpha'}\}$, which is the set theoretic difference $\{\phi_\alpha\} - \{\phi_\alpha\}$ and is therefore disjoint to $\{\phi_p\}$ (Table 1). The two operators F_{12} and $1/r_{12}$ are multiplied *first* and then the integration over electronic degrees of freedom is carried out. In this way, F_{12} eradicates or alleviates the singularity $1/r_{12}$ in the Hamiltonian analytically and thereby leads to the accelerated basis-set convergence of correlation energies. It should be understood that $F_{ij}^{\kappa\lambda}$, F_{ij}^{rs} and $F_{ij}^{m\alpha'}$ are defined analogously to $F_{ij}^{\alpha\beta}$ [eqn (14)] and $(F_{12}/r_{12})_{ij}^{pq}$ is antisymmetrized. The last term on the right-hand side still involves the sum of integrals over the index (α') that spans an infinite set. This term is evaluated by approximating the sum over $\{\phi_{\alpha'}\}$ as a sum over the CABS $\{\phi_{\alpha'}\}$, which is the finite set of virtual orbitals that is disjoint to $\{\phi_p\}$. Using a' , b' and a'_n to label the CABS indices, the last term of eqn (27) becomes

$$v_{m\alpha'}^{pq} F_{ij}^{m\alpha'} \stackrel{\text{CABS}}{=} v_{m\alpha'}^{pq} F_{ij}^{m\alpha'}. \quad (28)$$

Analogous transformations of special intermediates X , B and P produce two-electron integrals of operators F_{12}^2 , $[F_{12}, [\nabla_1^2 + \nabla_2^2, F_{12}]]$ and F_{12}^2/r_{12} respectively, whose analytical evaluation is relatively straightforward. Intermediate B requires extra attention: an earlier approach for evaluating this term involved integrals of the non-Hermitian operator $[\nabla_1^2 + \nabla_2^2, F_{12}]$ and relied on extended and generalized

Brillouin conditions (EBC and GBC).^{13,14,45} An alternative approach is to approximate the single commutators *via* the RI and avoid the use of EBC and GBC.⁴⁶ Both approaches result in sums over the complete basis set ($\{\phi_\kappa\}$) which are approximated by those over the orbital basis set and CABS ($\{\phi_p\} \cup \{\phi_a\}$). SMITH does not perform the algebraic manipulations required to evaluate these special intermediates. It instead detects them and suggests computational sequences on the basis of the assumption that they are available at runtime by an external integrals engine.

The sums over the complete basis set in other numerous terms are approximated by those over the CABS¹⁵ as in eqn (28). This process (the RI insertion) is automated by SMITH for the terms that are not special intermediates. In the next subsection, the automation of this step will be explained in more detail. The RI insertion with the CABS amounts to replacing an infinite sum by a finite sum:

$$\sum_{\alpha'} \stackrel{\text{CABS}}{=} \sum_{\alpha'}, \quad (29)$$

$$\sum_{\alpha} \stackrel{\text{CABS}}{=} \sum_a + \sum_{\alpha'}. \quad (30)$$

These replacements are equivalent to approximating the projector in eqn (13c) as

$$\hat{Q}_{12}^{(2)} \stackrel{\text{CABS}}{=} \hat{V}_1 \hat{P}'_2 + \hat{P}'_1 \hat{V}_2 + \hat{P}'_1 \hat{P}'_2, \quad (31)$$

where \hat{P}'_i is the projector on the CABS space.

B Automated derivation

The derivation step refers to the process of transforming the ansatz (written in terms of the expectation values of second-quantized operators in a Slater determinant) to a sum of product-tensor expressions, each optionally multiplied by index permutation operators. The derivation of the CC-R12 equations also involves the identification of the special intermediates, the RI insertions and an *ad hoc* common subexpression elimination of certain recurring intermediates. These steps have been completely automated by SMITH.

Previously, TCE carried out the automated derivation by applying Wick's theorem, *i.e.* by contracting normal-ordered strings of creation and annihilation operators. Unlike TCE, SMITH's algorithm uses antisymmetrized Goldstone diagrams and produces each topologically distinct term only once at every stage of the contraction process. The use of the diagrams makes SMITH considerably faster than TCE and, because CC-R12 is much more complex than CC at a given rank, this increased efficiency of algebraic manipulations is essential.

SMITH generates and interprets the diagrams according to the rules stipulated by Bartlett^{47,48} and extended to the CC-R12 ansätze, in which second-quantized operators are represented by vertices with single-arrow upgoing (particle), double-arrow upgoing (complete particle) and single-arrow downgoing (hole) lines. The numbers of lines above and below the vertices are respectively related to the excitation and deexcitation ranks of the operator. In SMITH, each vertex is computationally stored as a class object with attributes such as the vertex type and strings of creation or annihilation operators of particle,

complete particle and hole types. Interaction operators are compactly expressed by operators of unspecified types.

SMITH contracts creation and annihilation operators of the same type between all excitation vertices and an interaction vertex and spawns just the topologically distinct diagram fragments. This can be performed efficiently by using the symbolic algorithm^{47,48} that exhaustively enumerates distinct permutations of connectable lines and that can be straightforwardly computerized. The contraction step is repeated between the diagram fragments and deexcitation operators. The numerical factors and index permutation operators acting on the resulting tensor contraction expressions are determined by applying the established diagrammatic rules.^{47,48} The only new rule that is added for the CC-R12 ansätze is that when a creation (annihilation) operator of an unspecified type in an interaction vertex is contracted with an annihilation (creation) operator of a known type, the corresponding tensor index in the interaction vertex obtains the same (particle, complete particle or hole) operator type.

TCE could only handle ansätze restricted to a form

$$\langle \Phi_0 | (\hat{L} \hat{\Omega} \hat{R}_1 \cdots \hat{R}_n)_{\text{C,L}} | \Phi_0 \rangle \quad (32)$$

which contained one deexcitation \hat{L} operator, any number of excitation $\hat{R}_1 \cdots \hat{R}_n$ operators and one interaction (*i.e.* neither excitation nor deexcitation) $\hat{\Omega}$ operator, which could be variously connected or linked. In conjunction with a certain prescribed order of tensor contractions, these restrictions led to intermediates with *a priori* known highly symmetric index groups.^{25,28} These restrictions are lifted in SMITH, which can handle more general expectation values that have arbitrary numbers of deexcitation, excitation and general operators (and the corresponding tensors) such as eqn (16)–(19). Since the new operator added in the CC-R12 ansätze, $\hat{\mathcal{F}}$ [eqn (6)], is in fact an excitation operator, the CCSD-R12 ansatz eqn (16)–(19) may appear to be handled by TCE if Ft is treated as a compound tensor. The subsequent algebraic transformations (*vide infra*), however, must treat F and t independently when introducing the special intermediates into the equations. Furthermore, one of the special intermediates X has the form of an interaction operator, inserting itself as the second tensor of the type Ω in the computational sequence. Hence, the more general algorithms of SMITH reported here are crucial for the entire procedure.

The CCSD-R12 equations [eqn (16)–(19)] produced by SMITH are shown in Tables 2–5. The equations of CCSDT-R12 and CCSDTQ-R12 have also been derived and made available as ESI.† Although the CCSDT-R12 equations and computational sequences in the SA have been reported by Noga and Kutzelnigg,⁹ unabridged equations of these high-rank methods have not been documented before. These expressions involve P_n (not to be confused with the \hat{P}_n projectors), which is a shorthand notation of the operator that permutes n indices of the tensor upon which it acts. For instance, P_2 acting on the following contraction is expanded as

$$P_2 f_{a_8}^{a_3} v_{i_1 i_2}^{a_4 a_8} \equiv (1 - P_{a_3 a_4}) f_{a_8}^{a_3} v_{i_1 i_2}^{a_4 a_8} = f_{a_8}^{a_3} v_{i_1 i_2}^{a_4 a_8} - f_{a_8}^{a_4} v_{i_1 i_2}^{a_3 a_8} \quad (33)$$

where $P_{a_3 a_4}$ interchanges indices a_3 and a_4 wherever they appear to the right of the operator. The explicit form of P_n

Table 2 The left-hand side of the energy equation ($e = E_0$) of CCSD-R12 [eqn (16)] obtained with the modified ansatz 2

$$e = +f_{a_2}^{i_1} f_{i_1}^{a_2} + \frac{1}{2} v_{a_3 a_4}^{i_1 i_2} f_{i_1 i_2}^{a_3 a_4} + \frac{1}{4} v_{a_3 a_4}^{i_1 i_2} f_{i_1 i_2}^{a_3 a_4} + \frac{1}{8} v_{a_3 a_4}^{i_1 i_2} F_{i_9 i_{10}}^{a_3 a_4} f_{i_9 i_{10}}^{i_1 i_2}$$

is readily inferred from the tensor contraction expression, according to the rules written in ref. 47 and 48 and will not be shown here.

As eqn (6) suggests, the energy and T_1 and T_2 amplitude equations of CCSD-R12 add a new term containing the Ft tensor product at every appearance of the T_2 amplitude in the corresponding equations of CCSD. Although the geminal amplitude equation (Table 5) has no counterpart in CCSD, it resembles the T_2 amplitude equation because the $\hat{\mathcal{F}}$ operator is also a two-body excitation operator. Unlike the T amplitude equations, which become increasingly more lengthy as the rank of \hat{T} is raised, the complexity of the geminal amplitude equation increases only modestly with the rank of \hat{T} because the rank of $\hat{\mathcal{F}}$ is held fixed. Since only \hat{T}_n ($1 \leq n \leq 3$) can appear in the geminal amplitude equation in CC-R12 of any rank, the geminal amplitude equation remains the same for CCSDT-R12 and higher.

SMITH subsequently seeks the subexpressions that correspond to the special intermediates— V , X , B and P —and replaces them with the corresponding single tensor objects. This process involves matching the tensor types and contraction patterns in the equations against the definitions of these intermediates [eqn (23)–(26)]. Therefore, it occurs before the binary tensor contraction order is determined (*vide infra*). For instance, the second term in the right-hand side of the geminal amplitude equation of CCSD-R12 (Table 5) reads

$$+\frac{1}{4}(1 - P_{i_1 i_2}) F_{a_5 a_6}^{i_3 i_4} f_{i_1}^{i_7} F_{i_8 i_9}^{a_5 a_6} f_{i_2 i_7}^{i_8 i_9}. \quad (34)$$

SMITH uses eqn (24) to transform this into an expression,

$$-\frac{1}{2}(1 - P_{i_1 i_2}) f_{i_2}^{i_8 i_9} f_{i_1 i_7}^{i_8 i_9} X_{i_8 i_9}^{i_3 i_4}, \quad (35)$$

which is devoid of the indices associated with the complete basis set and hence is a programmable expression, provided that X is furnished by an external integrals engine.

Table 4 The left-hand side of the T_2 amplitude equation ($\delta_{i_2 i_1}^{a_3 a_4} = 0$) of CCSD-R12 [eqn (18)] obtained with the modified ansatz 2

$$\begin{aligned} \delta_{i_2 i_1}^{a_3 a_4} = & + P_2 f_{i_1}^{i_5} f_{i_2 i_5}^{a_3 a_4} - P_2 f_{a_5}^{i_3} f_{i_1 i_2}^{a_4 a_5} + \frac{1}{2} P_2 f_{a_5}^{i_3} F_{i_6 i_7}^{a_3 a_4} f_{i_1 i_2}^{i_6 i_7} + \frac{1}{2} P_2 f_{a_6}^{i_5} F_{i_7 i_8}^{a_3 a_4} f_{i_1 i_2}^{i_7 i_8} + P_2 f_{a_6}^{i_5} f_{i_1 i_2}^{a_3 a_4} + P_2 f_{a_6}^{i_5} f_{i_1 i_2}^{a_3 a_4} + v_{i_1 i_2}^{a_3 a_4} + P_2 f_{i_1 i_2}^{i_5 a_3} f_{i_5}^{a_4} + P_2 f_{i_1 a_5}^{a_3 a_4} f_{i_2}^{a_5} \\ & + \frac{1}{2} P_2 v_{i_1 i_2}^{i_5 a_3} f_{i_5}^{a_4} + P_2 P_2 v_{i_1 i_2}^{i_5 a_3} f_{i_5}^{a_4} + \frac{1}{2} P_2 v_{a_5 a_6}^{i_1 i_2} f_{i_1 i_2}^{a_3 a_4} + \frac{1}{2} v_{i_1 i_2}^{i_5 a_3} f_{i_5}^{a_4} - P_2 P_2 v_{i_1 a_6}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} v_{a_5 a_6}^{i_1 i_2} f_{i_1 i_2}^{a_3 a_4} + \frac{1}{2} P_2 P_2 v_{i_1 a_6}^{i_5 a_3} F_{i_7 i_8}^{a_3 a_4} f_{i_2}^{a_4} \\ & + \frac{1}{4} v_{a_5 a_6}^{i_1 i_2} F_{i_7 i_8}^{a_3 a_4} f_{i_1 i_2}^{i_7 i_8} + \frac{1}{2} P_2 P_2 v_{i_1 a_6}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 P_2 v_{i_1 a_6}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{2} P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 P_2 v_{i_1 a_7}^{i_5 a_3} f_{i_2}^{a_4} \\ & + \frac{1}{2} P_2 P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - P_2 P_2 v_{i_1 a_7}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 v_{i_1 a_7}^{i_5 a_3} f_{i_2}^{a_4} - P_2 P_2 v_{i_1 a_7}^{i_5 a_3} f_{i_2}^{a_4} \\ & - P_2 v_{i_1 a_7}^{i_5 a_3} f_{i_2}^{a_4} - P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{2} P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 P_2 v_{a_6 a_7}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} \\ & + \frac{1}{8} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + P_2 P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} \\ & - P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{2} P_2 P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{2} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{2} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} \\ & - \frac{1}{2} P_2 P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} + \frac{1}{4} v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{4} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} \\ & + \frac{1}{8} P_2 P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} - \frac{1}{8} P_2 v_{a_7 a_8}^{i_1 i_2} f_{i_1 i_2}^{i_5 a_3} f_{i_2}^{a_4} \end{aligned}$$

Table 3 The left-hand side of the T_1 amplitude equation ($\delta_{i_1}^{a_2} = 0$) of CCSD-R12 [eqn (17)] obtained with the modified ansatz 2

$$\begin{aligned} \delta_{i_1}^{a_2} = & + f_{i_1}^{a_2} - f_{i_1}^{i_3} f_{i_3}^{a_2} + f_{a_3}^{i_1} f_{i_1}^{a_3} - f_{a_4}^{i_1} f_{i_1}^{a_4} + f_{a_4}^{i_1} f_{i_1}^{a_4} - \frac{1}{2} f_{a_4}^{i_1} f_{i_1}^{a_4} f_{i_1}^{i_3} \\ & - v_{i_1 a_4}^{i_3} f_{i_3}^{a_4} + v_{i_1 a_5}^{i_3} f_{i_3}^{a_5} + v_{a_4 a_5}^{i_3} f_{i_3}^{a_4} - \frac{1}{2} v_{i_1 a_5}^{i_3} f_{i_3}^{a_4} - \frac{1}{2} v_{a_4 a_5}^{i_3} f_{i_3}^{a_4} \\ & + \frac{1}{4} v_{i_1 a_5}^{i_3} F_{i_6 i_7}^{a_4 a_5} f_{i_3 i_4}^{i_6 i_7} - \frac{1}{4} v_{a_4 a_5}^{i_3} F_{i_6 i_7}^{a_4 a_5} f_{i_3 i_4}^{i_6 i_7} - v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} \\ & + v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} - \frac{1}{2} v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} \\ & - \frac{1}{2} v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} - \frac{1}{4} v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} \\ & + \frac{1}{4} v_{a_5 a_6}^{i_3} f_{i_3}^{a_5} f_{i_1}^{a_6} f_{i_4}^{a_2} \end{aligned}$$

Another term in the same equation,

$$+\frac{1}{4} F_{a_5 a_6}^{i_3 i_4} v_{a_8 a_9}^{i_7 a_5} F_{i_{10} i_{11}}^{a_8 a_9} f_{i_1 i_2}^{i_{10} i_{11}} f_{i_7}^{a_6}, \quad (36)$$

is simplified to

$$+\frac{1}{2} F_{a_5 a_6}^{i_3 i_4} v_{i_8 i_9}^{i_7 a_5} f_{i_1 i_2}^{i_8 i_9} f_{i_7}^{a_6}, \quad (37)$$

using eqn (23), which still contains a complete-basis-set index (α_5). In the SA of Kutzelnigg and Klopper,¹³ this and copious other terms vanished by virtue of approximating the complete basis set by the orbital basis set. In this work, however, we document a less approximate alternative that evaluates the contributions from them using the CABS (*vide supra*). This step (the RI insertion) is achieved by acting $\hat{Q}_{12}^{(2)}$ of eqn (31) on \hat{F} and replacing the index pair $a_m \alpha_n$ by $a_m d'_n$ and the pair $\alpha_m \alpha_n$ by $a_m d'_n$, $d'_m a_n$ and $d'_m d'_n$, where d'_m labels a particle index in the CABS space. The above example is then transformed to

$$+\frac{1}{2} F_{a_5 a_6}^{i_3 i_4} v_{i_8 i_9}^{i_7 d'_5} f_{i_1 i_2}^{i_8 i_9} f_{i_7}^{a_6}, \quad (38)$$

which does not involve complete basis set indices and is subject to a computer implementation. In general, this step can spawn multiple terms from a single seed term. For instance, the following term containing complete-basis-set indices,

$$\frac{1}{8}(1 - P_{i_1 i_2}) F_{a_5 a_6}^{i_3 i_4} v_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_9 a_{10}} f_{i_1 i_7}^{i_{11} i_{12}} F_{i_3 i_4}^{a_9 a_{10}} f_{i_2 i_8}^{i_{11} i_{12}}, \quad (39)$$

is transformed to the sum of five terms without such indices as illustrated diagrammatically in Fig. 2.

At this stage, SMITH seeks and replaces every occurrence of the binary tensor products Ft by the special intermediate

Table 5 The left-hand side of the geminal t amplitude equation ($\delta_{i_2 i_1}^{i_3 i_4} = 0$) of CCSD-R12 [eqn (19)] obtained with the modified ansatz 2

$$\begin{aligned} \delta_{i_1 i_2}^{i_3 i_4} = & -F_{a_5 a_6}^{i_3 i_4} f_{a_7}^{i_1} t_{i_1 i_2}^{a_6 a_7} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} f_{i_1}^{i_7} F_{i_8 i_9}^{a_5 a_6} t_{i_2 i_7}^{i_8 i_9} + \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} f_{a_7}^{i_1} F_{i_8 i_9}^{a_5 a_7} t_{i_1 i_2}^{i_8 i_9} - \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} f_{i_7}^{i_1} F_{i_8 i_9}^{a_5 a_6} t_{i_1 i_2}^{i_8 i_9} - \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} f_{i_7}^{i_1} F_{i_8 i_9}^{a_5 a_8} t_{i_1 i_2}^{i_8 i_9} + \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} V_{i_1 i_2}^{a_5 a_6} \\ & + F_{a_5 a_6}^{i_3 i_4} V_{i_1 i_2}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_7} + \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_7}^{a_5 a_6} t_{i_1 i_2}^{a_7 a_8} + P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_8}^{a_5 a_6} t_{i_1 i_2}^{a_8 a_9} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_7 a_8}^{a_5 a_6} t_{i_1 i_2}^{a_7 a_8} - P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_8}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_8} + \frac{1}{4} F_{a_5 a_6}^{i_3 i_4} V_{a_7 a_8}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_8} \\ & + \frac{1}{8} F_{a_5 a_6}^{i_3 i_4} V_{i_1 i_2}^{i_7 i_8} F_{i_9 i_{10}}^{a_5 a_6} t_{i_1 i_2}^{i_9 i_{10}} + \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_8}^{i_7 a_6} F_{i_9 i_{10}}^{a_5 a_8} t_{i_1 i_2}^{i_9 i_{10}} + \frac{1}{8} F_{a_5 a_6}^{i_3 i_4} V_{a_7 a_8}^{i_7 a_6} F_{i_9 i_{10}}^{a_5 a_6} t_{i_1 i_2}^{i_9 i_{10}} + \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_9} - F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_9} \\ & + P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_9} + \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_5} t_{i_1 i_2}^{a_6 a_9} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_9}^{i_7 a_6} F_{i_{10} i_{11}}^{a_5 a_6} t_{i_1 i_2}^{i_{10} i_{11}} + \frac{1}{8} P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_9}^{i_7 i_8} F_{i_{10} i_{11}}^{a_5 a_6} t_{i_1 i_2}^{i_{10} i_{11}} - \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_6} F_{i_{10} i_{11}}^{a_5 a_8} t_{i_1 i_2}^{i_{10} i_{11}} \\ & - \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{i_1 a_9}^{i_7 i_8} F_{i_{10} i_{11}}^{a_5 a_9} t_{i_1 i_2}^{i_{10} i_{11}} + \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_6} F_{i_{10} i_{11}}^{a_5 a_8} t_{i_1 i_2}^{i_{10} i_{11}} + \frac{1}{4} F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_6} F_{i_{10} i_{11}}^{a_5 a_9} t_{i_1 i_2}^{i_{10} i_{11}} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_8 a_9}^{i_7 a_6} F_{i_{10} i_{11}}^{a_5 a_6} t_{i_1 i_2}^{i_{10} i_{11}} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} - \frac{1}{8} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} \\ & + \frac{1}{16} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} + \frac{1}{2} F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_9} t_{i_1 i_2}^{i_{11} i_{12}} + \frac{1}{4} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_9} t_{i_1 i_2}^{i_{11} i_{12}} - \frac{1}{8} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} \\ & + \frac{1}{16} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} - \frac{1}{4} F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_9} t_{i_1 i_2}^{i_{11} i_{12}} + \frac{1}{2} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} - \frac{1}{4} F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_9} t_{i_1 i_2}^{i_{11} i_{12}} \\ & + \frac{1}{8} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_9} t_{i_1 i_2}^{i_{11} i_{12}} - \frac{1}{8} F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} + \frac{1}{32} F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} \\ & - \frac{1}{16} P_2 F_{a_5 a_6}^{i_3 i_4} V_{a_9 a_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{a_5 a_6} t_{i_1 i_2}^{i_{11} i_{12}} \end{aligned}$$

denoted by \tilde{t} :

$$\tilde{t}_{i_1 i_2}^{d_5 d_4} = \frac{1}{2} F_{i_5 i_6}^{d_5 d_4} t_{i_1 i_2}^{i_5 i_6}, \quad (40)$$

$$\tilde{t}_{i_1 i_2}^{d_5 d_4} = \frac{1}{2} F_{i_5 i_6}^{d_5 d_4} t_{i_1 i_2}^{i_5 i_6}. \quad (41)$$

Unlike the other special intermediates, \tilde{t} intermediates do not need to be supplied by an external integrals engine but are readily evaluated as the right-hand sides of the above equations. They appear frequently throughout the CC-R12 equations and can be computed prior to the other contractions, stored and subsequently reused. This transformation can, therefore, be viewed as an example of common subexpression elimination which is automated for the other reusable intermediates (*vide infra*). This *ad hoc* transformation becomes necessary in CC-R12 because the search of optimal binary contraction orders in SMITH is non-exhaustive and this heuristic optimization reduces the operation cost of solving the CCSD-R12 geminal amplitude equations from $O(n_p^3 n_h^4)$ (with \tilde{t}) to $O(n_p^3 n_h^3)$ (with \tilde{t}). In this step, one of the terms that

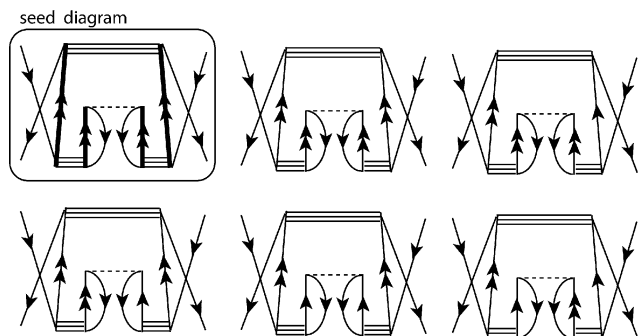


Fig. 2 One seed diagram (upper left) containing the complete-basis-set particle lines (bold lines with double going arrows) can spawn five individual diagrams that have no dependence on the complete basis set. In the latter, the complete-basis-set particle lines are replaced by those in the orbital basis set (thin lines with single going arrows) or those in the CABS (thin lines with double going arrows). The triple vertex may represent an Ft compound tensor.

arise from eqn (39) is transformed as follows:

$$\begin{aligned} & \frac{1}{8} (1 - P_{i_1 i_2}) F_{d_5 d_6}^{i_3 i_4} V_{d_9 d_{10}}^{i_7 i_8} F_{i_{11} i_{12}}^{d_5 d_6} t_{i_1 i_2}^{d_5 d_6} F_{i_{13} i_{14}}^{d_6 d_{10}} \\ & = \frac{1}{2} (1 - P_{i_1 i_2}) F_{d_5 d_6}^{i_3 i_4} V_{d_9 d_{10}}^{i_7 i_8} \tilde{t}_{i_1 i_2}^{d_5 d_6} \tilde{t}_{i_1 i_2}^{d_6 d_{10}}. \end{aligned} \quad (42)$$

SMITH automates all of the above steps, transforming the energy and amplitude equations of CCSD-R12 in Tables 2–5 into those shown in Tables ESI.3.I–III† and Table 6 respectively. The latter equations are considerably longer than the former, further supporting the argument for the use of a computerized symbolic algebra. They are in the spin-orbital formalisms and are not spin-adapted for any spin multiplicity. Computerizing the spin adaptation is a challenging symbol manipulation problem and is beyond the scope of this study. All the terms that involve F in the T amplitude equations (Tables ESI.3.I and ESI.3.II†) and a majority of those in the geminal amplitude equation (Table 6) vanish in the SA, tremendously simplifying the equations and subsequent computer implementations. Here we instead rely on the RI insertion using the CABS with the aim of achieving high accuracy with relatively small orbital basis sets.

C Computational sequences

The derived tensor expressions must be transformed into efficient computational sequences (*transformation*) before their implementations. SMITH performs three such algebraic transformation steps: the strength reduction, factorization and common subexpression elimination.

The first step (the strength reduction) solves the classic matrix chain multiplication problem approximately and determines the best *sequential* binary tensor contraction order, *e.g.* $A(B(CD))$, for each multiple tensor product, $ABCD$, where each letter denotes a tensor. Hence, it defines intermediates as binary tensor products: $\xi_1 = CD$ and $\xi_2 = B\xi_1$. While the result of a tensor product does not depend on the order of contraction owing to the associative and commutative nature of tensor contractions, the operation and memory costs can vary greatly. SMITH examines all $n!/2$ distinct sequential binary tensor contraction orders for an n -tuple product and finds the least expensive order by first comparing peak operation costs and then peak memory costs.

Table 6 The left-hand side of the geminal t amplitude equation ($\delta_{i_2 i_1}^{i_3 i_4} = 0$) of CCSD-R12 [eqn (19)] with the special intermediates [eqn (23)–(26)] and the RI insertion using the CABS [eqn (31)]

$$\begin{aligned}
 \delta_{i_1 i_2}^{i_3 i_4} = & + F_{a_7 a_6}^{i_3 i_4 *} J_{a_5}^{a_7} \tilde{v}_{i_1 i_2}^{a_5 a_6} + \frac{1}{2} P_2 X_{i_6 i_7}^{i_3 i_4} \tilde{v}_{i_2 i_5}^{i_6 i_7} \tilde{v}_{i_1}^{i_5} + \frac{1}{2} P_2 B_{i_5 i_6}^{i_3 i_4} \tilde{v}_{i_1 i_2}^{i_5 i_6} - \frac{1}{2} P_2 J_{a_8 i_2}^{i_7 a_8} \tilde{v}_{i_1 i_7}^{i_5 i_6} X_{i_5 i_6}^{i_3 i_4} - \int_{a_8}^{i_7} \tilde{v}_{i_1 i_2}^{a_5 a_6} \tilde{v}_{i_7}^{a_6} F_{a_5 a_6}^{i_3 i_4 *} - \int_{a_8}^{i_7} \tilde{v}_{i_1 i_2}^{a_5 a_6} \tilde{v}_{i_7}^{a_6} F_{a_5 a_6}^{i_3 i_4 *} - \int_{a_8}^{i_7} \tilde{v}_{i_1 i_2}^{a_5 a_6} \tilde{v}_{i_7}^{a_6} F_{a_5 a_6}^{i_3 i_4 *} + (V^\dagger)_{i_1 i_2}^{i_3 i_4} + F_{a_6 a_7}^{i_3 i_4 *} \tilde{v}_{i_5}^{i_6} \tilde{v}_{i_1 i_2}^{a_5 a_6} \\
 & - P_2 (V^\dagger)_{i_2 a_5}^{i_3 i_4} \tilde{v}_{i_1}^{a_5} - P_2 F_{a_7 a_8}^{i_3 i_4 *} \tilde{v}_{i_2 a_5}^{i_6} \tilde{v}_{i_1}^{a_5} + \frac{1}{2} P_2 (V^\dagger)_{a_5 a_6}^{i_3 i_4} \tilde{v}_{i_2}^{a_6} \tilde{v}_{i_1}^{a_5} + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} (V^\dagger)_{a_5 a_6}^{i_3 i_4} \tilde{v}_{i_2}^{a_6} \tilde{v}_{i_1}^{a_5} + \frac{1}{4} \tilde{v}_{i_1 i_2}^{i_7 i_8} \tilde{v}_{i_1 i_8}^{i_5 i_6} X_{i_5 i_6}^{i_3 i_4} - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & + \frac{1}{8} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{8} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{8} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{8} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - \frac{1}{4} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{8} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} \\
 & - \frac{1}{2} \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_8}^{a_6 a_7} F_{a_5 a_6}^{i_3 i_4 *} + \frac{1}{8} X_{i_9 i_10}^{i_3 i_4} \tilde{v}_{i_1 i_9}^{i_5 i_6} \tilde{v}_{i_2 i_10}^{i_5 i_6} - \frac{1}{4} P_2 \tilde{v}_{i_2 a_7}^{i_8 a_5} \tilde{v}_{i_1 i_9}^{i_5 i_6} X_{i_5 i_6}^{i_3 i_4}
 \end{aligned}$$

Non-sequential contraction orders, e.g. $(AB)(CD)$, are not considered in SMITH (or in TCE). While this limitation hardly affects the operation cost in CC, it turns out to be significant in CC-R12. The optimal *sequential* contraction order exhibits one-rank-higher polynomial size dependence of the operation cost than the optimal *non-sequential* contraction order. Since the geminal amplitude equations (with Ft viewed as two-electron excitation operators) have the structure similar to that of the T_2 amplitude equations, we may expect that, when the non-sequential contractions involving Ft are taken into consideration, the complexity of the geminal amplitude equations cannot scale more steeply than that of the corresponding T_2 amplitude equations. The aforementioned \tilde{t} transformation amounts to a practical way of allowing non-sequential contraction orders that are expected to be particularly important.

Previously, TCE performed the strength reduction similarly for the methods definable by eqn (32). It also examined all sequential contraction orders comparing their operation and memory costs, but permitted binary contraction orders were restricted to the form $L(R_i(\cdot \cdot (R_j \Omega) \cdot \cdot))$, where we used the same alphabets for the tensors and operators. This restriction was crucial to ensure that every resulting intermediate possessed an *a priori* known index permutation symmetry. With SMITH, any combination of excitation, deexcitation and general operators is permitted and there is no restriction in the binary contraction orders. The index permutation symmetry of the resulting intermediates is determined on a case-by-case basis automatically from the computational representations of the intermediates.

For instance, one of the terms in the geminal amplitude equation reads

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = -(1 - P_{i_1 i_2}) v_{i_2 a_7}^{i_8 a_6} \tilde{t}_{(i_1 i_8)}^{(a_5 a_7)} F_{(a_5 a_6)}^{(i_3 i_4)*}, \quad (43)$$

where some indices are parenthesized to show that they are permutable. All covariant (contravariant) indices of an input (F^\dagger , \tilde{t} and v in this equation) or output tensor (δ) are permutable unless they belong to different index classes: hole (i_n), particle (a_n), or CABS (d_n). For instance, $F_{(a_5 a_6)}^{(i_3 i_4)*}$ is anti-

symmetric with respect to the interchange of i_3 and i_4 or that of a_5 and a_6 , i.e.,

$$F_{a_5 a_6}^{i_3 i_4 *} = -F_{a_5 a_6}^{i_4 i_3 *} = -F_{a_6 a_5}^{i_3 i_4 *} = F_{a_6 a_5}^{i_4 i_3 *}. \quad (44)$$

Therefore, only those elements of δ , F^\dagger and \tilde{t} whose indices satisfy the following inequalities need to be stored: $F_{a_5 < a_6}^{i_3 < i_4 *}$,

$\delta_{i_1 < i_2}^{i_3 < i_4}$ and $\tilde{t}_{i_1 < i_8}^{a_5 < a_7}$. It is critical to exploit the index permutation symmetry to minimize the memory and operation costs of solving the amplitude equations. Furthermore, the block sparsity of the tensors that arises from the spatial symmetry and spin integration (within the spin-orbital formalisms) is also significant. These details of the computerized implementations are, however, deferred to our forthcoming article.

The binary contraction order for eqn (43) determined by SMITH is as follows:

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = \frac{1}{2} F_{(a_5 a_6)}^{(i_3 i_4)*} \zeta_{(i_1 i_2)}^{(a_5 a_6)}, \quad (45)$$

$$\zeta_{(i_1 i_2)}^{(a_5 a_6)} = -(1 - P_{i_1 i_2})(1 - P_{a_5 a_6}) v_{i_2 a_7}^{i_8 a_6} \tilde{t}_{(i_1 i_8)}^{(a_5 a_7)}. \quad (46)$$

The numerical factors (including the signs) in these individual equations are arbitrary insofar as their products are consistent with the overall numerical factor in eqn (43). The index permutation symmetry of the intermediate is indicated by parentheses. The general rule that determines the index permutation symmetry of intermediates can be stated as follows: (i) only like indices are permutable (covariant vs. contravariant; particle, hole and CABS); (ii) the indices that originate from one input tensor are permutable; (iii) the indices that will be contracted with those of one input tensor are permutable; (iv) the external indices (i.e. the indices of δ) are permutable.

In the above example, the indices i_1 and i_2 of $\zeta_{(i_1 i_2)}^{(a_5 a_6)}$ are permutable because they are the external indices [rule (iv)]. The indices a_5 and a_6 of $\zeta_{(i_1 i_2)}^{(a_5 a_6)}$ are permutable according to rule (iii) as they are both contracted to the permutable indices

in $F_{(a'_5 a'_6)}^{(i_3 i_4)*}$. The two permutation operators in eqn (46) ensure the desired antisymmetry of $\xi_{(i_1 i_2)}^{(a'_5 a'_6)}$. The insertion of the antisymmetrization operator $(1 - P_{a'_5 a'_6})$, which cannot be seen in eqn (43), is justifiable because $v_{i_2 a'_7}^{i_8 a'_6} \tilde{t}_{(i_1 i_8)}^{(a'_5 a'_7)}$ can be written as a sum of symmetric and antisymmetric components with respect to the interchange of a'_5 and a'_6 , and the symmetric component only gives rise to a vanishing contribution in eqn (45) because $F_{(a'_5 a'_6)}^{(i_3 i_4)*}$ is antisymmetric.

The second algebraic transformation step is the factorization. By virtue of the distributive nature of tensor algebra, common tensor contractions can be factorized, e.g. $AB + AC = A(B + C)$, defining intermediates as a sum of unary tensor expressions and/or binary tensor contractions. For instance, the sum of two tensor contractions,

$$\begin{aligned} \delta_{(i_1 i_2)}^{(i_3 i_4)} = & -(1 - P_{i_1 i_2}) v_{i_2 a'_7}^{i_8 a'_6} \tilde{t}_{(i_1 i_8)}^{(a'_5 a'_7)} F_{(a'_5 a'_6)}^{(i_3 i_4)*} \\ & + (1 - P_{i_1 i_2}) v_{(a_7 a_9)}^{i_8 a'_6} t_{i_2}^{a_9} \tilde{t}_{(i_1 i_8)}^{a_7} F_{(a'_5 a'_6)}^{(i_3 i_4)*} \end{aligned} \quad (47)$$

is evaluated by the following sequence:

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = \frac{1}{2} F_{(a'_5 a'_6)}^{(i_3 i_4)*} \left[\xi_{(i_1 i_2)}^{(a'_5 a'_6)} + \eta_{(i_1 i_2)}^{(a'_5 a'_6)} \right], \quad (48)$$

$$\eta_{(i_1 i_2)}^{(a'_5 a'_6)} = (1 - P_{i_1 i_2})(1 - P_{a'_5 a'_6}) \tilde{t}_{(i_1 i_8)}^{a_7} \Xi_{i_2 a_7}^{i_8 a'_6}, \quad (49)$$

$$\Xi_{i_2 a_7}^{i_8 a'_6} = v_{(a_7 a_9)}^{i_8 a'_6} t_{i_2}^{a_9}, \quad (50)$$

where ξ is defined in eqn (46). The factorization has replaced two matrix multiplications and one summation $F\xi + F\eta$ by one multiplication and one summation $F(\xi + \eta)$ in eqn (48). This step must be preceded by reexpressing the tensor contractions and their indices in a canonical order, which brings equivalent tensor contractions into literal identical expressions, so that the subsequent factorization can exhaustively locate all factorizable common multipliers. The canonical order is arbitrary but must be unambiguous and uniquely defined for each tensor contraction. The strength reduction and factorization are, in principle, a coupled optimization which is evidently an NP-hard (nondeterministic polynomial-time hard) problem. SMITH handles them as uncoupled, sequential optimizations.

The third algebraic transformation is the common sub-expression elimination. Take the contraction

$$+(1 - P_{i_1 i_2}) v_{(a_8 a_9)}^{i_7 a'_5} t_{i_2}^{a_9} t_{i_1}^{a_8} t_{i_7}^{a_6} F_{a'_5 a_6}^{(i_3 i_4)*} \quad (51)$$

as an example. SMITH suggests that this be evaluated in the following sequence:

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = F_{a'_5 a_6}^{(i_3 i_4)*} \zeta_{(i_1 i_2)}^{a'_5 a_6}, \quad (52)$$

$$\zeta_{(i_1 i_2)}^{a'_5 a_6} = t_{i_7}^{a_6} \tau_{(i_1 i_2)}^{i_7 a'_5}, \quad (53)$$

$$\tau_{(i_1 i_2)}^{i_7 a'_5} = (1 - P_{i_1 i_2}) t_{i_1}^{a_8} \Xi_{i_2 a_8}^{i_7 a'_5}, \quad (54)$$

$$\Xi_{i_2 a_8}^{i_7 a'_5} = v_{(a_8 a_9)}^{i_7 a'_5} t_{i_2}^{a_9}, \quad (55)$$

where the equivalence of the two intermediates defined by eqn (50) and (55) is implied by the use of the common symbol Ξ . This Ξ intermediate, therefore, can be computed only once, stored and reused, unlike other volatile intermediates that are used only once and discarded afterward. SMITH examines the whole computational sequences, inspecting the tensors and their contractions, and identifies reusable intermediates. This optimization is relatively unimportant in CC, ²⁷ but there are some expensive reusable intermediates in the geminal amplitude equation of CC-R12 (e.g. Ξ_7 in Table 7). However, the most important reusable intermediate is \tilde{t} , which is introduced in an *ad hoc* fashion and significantly reduces the peak operation cost of CCSD-R12 when carried out prior to the strength reduction. The reusable intermediates occur not just at the terminal positions of the tree-like structure of the computational sequences but also at the non-terminal positions.

The computational sequences and intermediates for the T_1 , T_2 and geminal t amplitude equations of CCSD-R12 suggested by SMITH are given in Tables ESI.4.I and ESI.4.II† and in Table 7, in which ξ and Ξ symbolize volatile and reusable intermediates respectively. The permutable indices are not identified in these Tables, although this information is maintained internally in the computational representations of the intermediates. The binary contraction order is determined by assuming that $n_h = 28$, $n_p = 232$ and $n_{p'} = 888$ (the numbers of occupied orbitals, virtual orbitals and CABS respectively), which correspond to a calculation for ethylene using aug-cc-pVTZ for the orbital basis set and [15s9p7d5f/9s7p5d] for the auxiliary basis set. The suggested computational sequences and intermediates may vary considerably with these parameters.

The peak operation cost of evaluating the right-hand side of the CCSD-R12 geminal amplitude equation is $O(n_p^3 n_h^3)$. This cost has the same polynomial rank as that of the T_2 amplitude equation of conventional CCSD [$O(n_p^4 n_h^2)$] as well as the cost of computing the special intermediates, but the former has a much greater prefactor and is estimated to be an order of magnitude greater than the latter two for realistic choices of n_h , n_p and $n_{p'}$ such as the above. This fact may support approximations which neglect these expensive terms such as SA ¹³ and various approximate CC-R12 schemes. ^{18,20,23,24} Another way to reduce the overall cost of CCSD-R12 is *via* the weak orthogonality projectors, ^{49–52} which eliminate the integrals of the highest dimensionality from the geminal amplitude equation. Yet another method is to group and order the terms according to the operation and memory costs and truncate the equation to maximize the cost performance. With SMITH, the latter strategy and various other systematic approximations can be relatively easily explored.

Unlike the T amplitude equations, the geminal amplitude equation does not become exponentially more complex with the rank of \hat{T} (Table 8). In fact, the CCSDT-R12 geminal

Table 7 The computational sequence and intermediates for the geminal t amplitude equation of CCSD-R12 [eqn (19)]

$(\Xi_0)_{i_7 a_6}^{i_3 i_4} = + t_{i_7}^{a_9} F_{a_6 a_9}^{i_3 i_4 *}$	$(\zeta_{3,5})_{a_7}^{a_6} = -t_{i_9}^{a_8} v_{a_7 a_8}^{i_9 a_6} - \frac{1}{2} t_{i_9 i_{10}}^{a_6 a_8} v_{a_7 a_8}^{i_9 i_{10}} + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{a_8 a_6} v_{a_7 a_8}^{i_9 i_{10}}$
$(\Xi_1)_{i_2 a_7}^{i_8 a_6} = + t_{i_2}^{a_9} v_{a_7 a_9}^{i_8 a_6}$	$(\zeta_{3,4})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + t_{i_2}^{a_9} v_{a_7 a_9}^{i_8 a_6} + t_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}} + \tilde{t}_{i_2 i_{10}}^{a_9 a_6} v_{a_7 a_9}^{i_8 i_{10}}$
$(\Xi_2)_{a_6}^{a_7} = + t_{i_9}^{a_8} v_{a_6 a_8}^{i_9 a_7}$	$(\zeta_{3,3})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6}$
$(\Xi_3)_{a_7}^{a_5} = + t_{i_9}^{a_8} v_{a_7 a_8}^{i_9 a_5}$	$(\zeta_{3,2})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + t_{i_2}^{a_9} v_{a_7 a_9}^{i_8 a_6} - \tilde{t}_{i_2 i_{10}}^{a_9 a_6} v_{a_7 a_9}^{i_8 i_{10}}$
$(\Xi_4)_{i_2 a_7}^{i_8 a_5} = + t_{i_2}^{a_9} v_{a_7 a_9}^{i_8 a_5}$	$(\zeta_{3,1})_{i_2 a_7}^{i_8 a_5} = + v_{i_2 a_7}^{i_8 a_5} - (\Xi_1)_{i_2 a_7}^{i_8 a_5} + (\Xi_7)_{i_2 a_7}^{i_8 a_5}$
$(\Xi_5)_{a_8}^{i_7} = + t_{i_{10}}^{a_9} v_{a_8 a_9}^{i_7 i_{10}}$	$(\zeta_{3,0,3})_{i_2 a_8}^{i_7 i_9} = -v_{i_2 a_8}^{i_7 i_9} + (\Xi_6)_{i_2 a_8}^{i_7 i_9}$
$(\Xi_6)_{i_2 a_8}^{i_7 i_9} = + t_{i_2}^{a_{10}} v_{a_8 a_{10}}^{i_7 i_9}$	$(\zeta_{3,0,2})_{i_2 a_8}^{i_7 i_9} = -v_{i_2 a_8}^{i_7 i_9} + t_{i_2}^{a_{10}} v_{a_8 a_{10}}^{i_7 i_9}$
$(\Xi_7)_{i_2 a_7}^{i_8 a_6} = + \tilde{t}_{i_2 i_{10}}^{a_6 a_7} v_{a_7 a_8}^{i_8 i_{10}}$	$(\zeta_{3,0,0})_{a_8}^{i_7} = -J_{a_8}^{i_7} - t_{i_{10}}^{a_9} v_{a_8 a_9}^{i_7 i_{10}}$
$(\Xi_8)_{a_6}^{a_7} = + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{a_7 a_6} v_{a_6 a_6}^{i_9 i_{10}}$	$(\zeta_{3,0})_{i_{12}}^{i_7 a_5} = + \tilde{t}_{i_{12}}^{a_5 a_6} (\zeta_{3,0,0})_{a_6}^{i_7} + \frac{1}{2} P_2 t_{i_1}^{a_8} (\Xi_1)_{i_2 a_8}^{i_7 a_5} + P_2 \tilde{t}_{i_1 i_9}^{a_5 a_8} (\zeta_{3,0,2})_{i_2 a_8}^{i_7 i_9}$
$(\Xi_9)_{a_6}^{a_7} = + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{a_5 a_8} v_{a_6 a_8}^{i_9 i_{10}}$	$+ P_2 \tilde{t}_{i_1 i_9}^{a_5 a_8} (\zeta_{3,0,3})_{i_2 a_8}^{i_7 i_9} - \tilde{t}_{i_{12}}^{a_5 a_8} (\Xi_5)_{a_8}^{i_7}$
$(\Xi_{10})_{a_7}^{a_5} = + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{a_5 a_8} v_{a_7 a_8}^{i_9 i_{10}}$	$(\zeta_{3,1})_{i_{12}}^{a_5 a_6} = + t_{i_7}^{a_6} (\zeta_{3,0})_{i_{12}}^{i_7 a_5} + P_2 t_{i_1 i_8}^{a_6 a_7} (\zeta_{3,1})_{i_2 a_7}^{i_8 a_5} + P_2 \tilde{t}_{i_1 i_2}^{a_5 a_7} (\zeta_{3,2})_{i_2 a_7}^{i_8 a_6}$
$(\Xi_{11})_{a_7}^{a_5} = + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{a_5 a_8} v_{a_7 a_8}^{i_9 i_{10}}$	$+ P_2 \tilde{t}_{i_1 i_8}^{a_7 a_6} (\zeta_{3,3})_{i_2 a_7}^{i_8 a_5} + P_2 \tilde{t}_{i_1 i_8}^{a_5 a_7} (\zeta_{3,4})_{i_2 a_7}^{i_8 a_6} + \tilde{t}_{i_{12}}^{a_5 a_7} (\zeta_{3,5})_{a_7}^{a_6}$
$(\zeta_{8,2})_{a_7}^{a_6} = -(\Xi_3)_{a_7}^{a_6} - (\Xi_{10})_{a_7}^{a_6} - (\Xi_{11})_{a_7}^{a_6}$	$+ \tilde{t}_{i_{12}}^{a_5 a_6} (\zeta_{3,6})_{a_7}^{a_6} + \tilde{t}_{i_{12}}^{a_5 a_7} (\zeta_{3,7})_{a_7}^{a_6}$
$(\zeta_{8,1})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_1)_{i_2 a_7}^{i_8 a_6} - (\Xi_7)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{2,1})_{i_5 i_6}^{i_7 i_8} = + \frac{1}{2} \tilde{t}_{i_9 i_{10}}^{i_7 i_8} v_{i_5 i_6}^{i_9 i_{10}}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{2,0})_{i_5 i_6}^{i_3 i_4} = + P_{i_5 i_6}^{i_3 i_4} + P_{i_5 i_6}^{i_3 i_4} + V_{i_5 i_6}^{i_7 i_8} (\Xi_0)_{i_7 a_8}^{i_3 i_4} + \frac{1}{2} X_{i_7 i_8}^{i_3 i_4} (\zeta_{2,1})_{i_5 i_6}^{i_7 i_8}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{1,1,0})_{i_2 a_9}^{i_7 i_8} = -v_{i_2 a_9}^{i_7 i_8} + \frac{1}{2} (\Xi_6)_{i_2 a_9}^{i_7 i_8}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{1,1})_{i_1 i_2}^{i_7 i_8} = + P_2 t_{i_1}^{a_9} (\zeta_{1,1,0})_{i_2 a_9}^{i_7 i_8} + \frac{1}{2} \tilde{t}_{i_1 i_2}^{a_9 a_{10}} v_{a_9 a_{10}}^{i_7 i_8}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{1,0,0})_{a_8}^{i_7} = -J_{a_8}^{i_7} - (\Xi_5)_{a_8}^{i_7}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{1,0})_{i_2}^{i_7} = -J_{i_2}^{i_7} + t_{i_2}^{a_8} (\zeta_{1,0,0})_{a_8}^{i_7} - t_{i_9}^{a_8} v_{i_2 a_8}^{i_7 i_9} - \frac{1}{2} t_{i_2 i_{10}}^{a_8 a_9} v_{a_8 a_9}^{i_7 i_{10}} - \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{i_8 i_9} v_{i_2 a_8}^{i_7 i_{10}}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{1,1})_{i_1 i_2}^{i_5 i_6} = + P_2 t_{i_1 i_7}^{i_5 i_6} (\zeta_{1,0})_{i_2}^{i_7} + \frac{1}{2} \tilde{t}_{i_7 i_8}^{i_5 i_6} (\zeta_{1,1})_{i_1 i_2}^{i_7 i_8}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{0,0})_{a_6}^{a_7} = -J_{a_6}^{a_7} + (\Xi_2)_{a_6}^{a_7} - (\Xi_8)_{a_6}^{a_7} + (\Xi_9)_{a_6}^{a_7}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{0,0})_{a_6}^{a_7} = -J_{a_6}^{a_7} + (\Xi_2)_{a_6}^{a_7} - (\Xi_8)_{a_6}^{a_7} + (\Xi_9)_{a_6}^{a_7}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$(\zeta_{0,0})_{a_5 a_6}^{i_3 i_4} = + (V^\dagger)_{a_5 a_6}^{i_3 i_4} + P_2 F_{a_7 a_5}^{i_3 i_4 *} (\zeta_{0,0})_{a_6}^{a_7} + v_{a_5 a_6}^{i_7 a_6} (\Xi_0)_{i_7 a_8}^{i_3 i_4}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$\delta_{i_1 i_2}^{i_3 i_4} = + (V^\dagger)_{i_1 i_2}^{i_3 i_4} + \frac{1}{2} t_{i_1 i_2}^{a_5 a_6} (\zeta_{0,0})_{a_5 a_6}^{i_3 i_4} + \frac{1}{2} X_{i_5 i_6}^{i_3 i_4} (\zeta_{1,1})_{i_1 i_2}^{i_5 i_6} + \frac{1}{2} \tilde{t}_{i_1 i_2}^{i_5 i_6} (\zeta_{2,0})_{i_5 i_6}^{i_3 i_4}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$+ F_{a_5 a_6}^{i_3 i_4 *} (\zeta_{3,1})_{i_1 i_2}^{a_5 a_6} + \tilde{t}_{i_1 i_2}^{a_5 a_6} (\zeta_{4,1})_{i_1 i_2}^{i_3 i_4} + v_{i_5 a_6}^{i_5 a_6} (\Xi_0)_{i_5 a_6}^{i_3 i_4} + P_2 t_{i_1}^{a_5} (\zeta_{5,6})_{i_2 a_6}^{i_3 i_4}$
$(\zeta_{8,0})_{i_2 a_7}^{i_8 a_6} = -v_{i_2 a_7}^{i_8 a_6} + (\Xi_4)_{i_2 a_7}^{i_8 a_6} + \frac{1}{2} \tilde{t}_{i_2 i_{10}}^{a_6 a_9} v_{a_7 a_9}^{i_8 i_{10}}$	$+ \frac{1}{2} v_{i_1 i_2}^{i_5 i_6} (\zeta_{7,1})_{i_5 i_6}^{i_3 i_4} + \frac{1}{2} F_{a_5 a_6}^{i_3 i_4 *} (\zeta_{8,1})_{i_1 i_2}^{a_5 a_6}$

amplitude equation adds only one term (see Fig. 3 for its diagrammatic representation),

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = \frac{1}{2} F_{a_5 a_6}^{(i_3 i_4)*} t_{(i_1 i_2 i_9)}^{(a_6 a_7 a_8)} v_{(a_7 a_8)}^{i_9 a_5} \quad (56)$$

to the corresponding equation of CCSD-R12. This can be evaluated in two contraction steps,

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = F_{a_5 a_6}^{(i_3 i_4)*} \zeta_{(i_1 i_2)}^{a_5 a_6} \quad (57)$$

$$\zeta_{(i_1 i_2)}^{a_5 a_6} = \frac{1}{2} t_{(i_1 i_2 i_9)}^{(a_6 a_7 a_8)} v_{(a_7 a_8)}^{i_9 a_5} \quad (58)$$

at an overall $O(n_p n_p^3 n_h^3)$ cost. While this may be less than the $O(n_p^3 n_h^3)$ cost of other terms already present in CCSD-R12 for

small basis sets, it eventually outgrows the rest and becomes the dominant term in the geminal amplitude equation as the basis set sizes increase. Nevertheless, the complexity of the T amplitude equations also rises considerably from $O(n_p^4 n_h^2)$ (CCSD-R12) to $O(n_p^5 n_h^3)$ (CCSDT-R12) and, consequently, the cost of solving the geminal amplitude equation is expected to be marginal when compared to that of solving the T amplitude equations in CCSDT-R12. With the above combination of n_h , n_p and n_p' , the geminal amplitude equation costs two orders of magnitude less than the T amplitude equation. The ratio becomes even smaller as the basis sets are extended and/or the rank of \hat{T} is raised. Therefore, approximating the geminal amplitude equation at the sacrifice of accuracy may not be justifiable in CCSDT-R12 and higher-ranked methods.

Table 8 The size dependence of the peak operation costs of solving the geminal amplitude equations and T , Λ , R or L amplitude equations of the CC-R12 methods of rank k

Method	Geminal	T , Λ , R or L
EOM- (right) and CC-R12 ($k = 2$)	$O(n_p^3 n_h^3)$	$O(n_p^{k+2} n_h^k)$
EOM- (right) and CC-R12 ($k \geq 3$)	$O(n_p n_p^3 n_h^3)$	$O(n_p^{k+2} n_h^k)$
EOM- (left) and Λ -CC-R12 ($k = 2$)	$O(n_p^3 n_h^3)$	$O(n_p^3 n_h^3)$
EOM- (left) and Λ -CC-R12 ($k \geq 3$)	$O(n_p^{k+1} n_h^{k+1})$	$O(n_p^{k+2} n_h^k)$

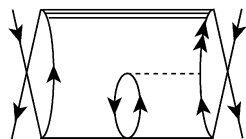


Fig. 3 The diagrammatic representation of eqn (56).

Unlike the conventional CC methods, in which the implementation effort can be focused on only one diagrammatic term that dominates the overall operation cost, the CC-R12 equations typically include multiple terms with comparable operation costs. Furthermore, the costs of these terms depend on three parameters (n_n , n_p and $n_{p'}$) instead of two and their relative importance becomes much harder to comprehend. Efficient computer implementation of even the ground-state CC-R12 method poses an intractably complex optimization problem that can be tackled robustly only with a computerized symbolic algebra such as SMITH.

III. EOM- and Λ -CC-R12 equations

Our computerized symbolic algebra can also be applied directly to excited-state CC-R12 methods *via* the EOM-CC formalism. They parametrize the n th excited right-hand-side wave function as

$$|\Psi_n\rangle = \hat{R}^{[n]}|\Psi_0\rangle = \exp(\hat{S})\hat{R}^{[n]}|\Phi_0\rangle, \quad (59)$$

where $\hat{R}^{[n]}$ is an excitation operator that commutes with \hat{S} . For EOM-CCSD-R12, it is

$$\hat{R}^{[n]} = \hat{R}_0^{[n]} + \hat{R}_1^{[n]} + \hat{R}_2^{[n]} + \hat{\mathcal{R}}^{[n]}, \quad (60)$$

in which the first term is a constant and the second through fourth terms are the following:

$$\hat{R}_1^{[n]} = (r^{[n]})_i^a \{a^\dagger i\}, \quad (61)$$

$$\hat{R}_2^{[n]} = \frac{1}{4}(r^{[n]})_{ij}^{ab} \{a^\dagger b^\dagger ji\}, \quad (62)$$

and

$$\hat{\mathcal{R}}^{[n]} = [\hat{F}\hat{r}^{[n]}]_C = \frac{1}{8}F_{kl}^{\alpha\beta}(r^{[n]})_{ij}^{kl} \{\alpha^\dagger \beta^\dagger ji\}, \quad (63)$$

with

$$r^{[n]} = \frac{1}{4}(r^{[n]})_{ij}^{kl} \{k^\dagger l^\dagger ji\}, \quad (64)$$

where the excited-state index “[n]” will be omitted whenever it is not essential. In eqn (63), F and $r^{[n]}$ must be diagrammatically connected through both k and l lines. Substituting eqn (59) into the Schrödinger equation and projecting it onto the determinant space accessible by the action of $\hat{R}^{[n]}$ on $|\Phi_0\rangle$, we arrive at the EOM-CCSD-R12 equations for the right-hand-side wave function and excitation energy $\omega^{[n]}$, *i.e.*

$$\langle \Phi_i^a | (\bar{H}\hat{R}^{[n]})_C | \Phi_0 \rangle = \omega^{[n]}(r^{[n]})_i^a, \quad (65)$$

$$\langle \Phi_{ij}^{ab} | (\bar{H}\hat{R}^{[n]})_C | \Phi_0 \rangle = \omega^{[n]}(r^{[n]})_{ij}^{ab}, \quad (66)$$

and

$$\langle \Phi_{ij}^{kl} | (\bar{H}\hat{R}^{[n]})_C | \Phi_0 \rangle = \frac{1}{2}\omega^{[n]}X_{mn}^{kl}(r^{[n]})_{ij}^{mn}, \quad (67)$$

where special intermediate X is defined in eqn (24). Owing to the connectedness, $\hat{R}_0^{[n]}$ does not appear in these equations. They have a trivial, ground-state solution: $\hat{\mathcal{R}}_0^{[0]} = 1$, $\hat{R}_1^{[0]} = \hat{\mathcal{R}}_0^{[0]} = 0$, and $\omega^{[0]} = 0$.

The left-hand-side wave function of EOM-CCSD-R12 is written as

$$\langle \Psi_n | = \langle \Phi_0 | \hat{L}^{[n]} \exp(-\hat{S}), \quad (68)$$

where $\hat{L}^{[n]} = \hat{L}_0^{[n]} + \hat{L}_1^{[n]} + \hat{L}_2^{[n]} + \hat{\mathcal{L}}^{[n]}$ is a deexcitation operator, whose components are defined as

$$\hat{L}_1^{[n]} = (l^{[n]})_a^i \{i^\dagger a\}, \quad (69)$$

$$\hat{L}_2^{[n]} = \frac{1}{4}(l^{[n]})_{ab}^{ij} \{i^\dagger j^\dagger ba\}, \quad (70)$$

$$\hat{\mathcal{L}}^{[n]} = [\hat{l}^{[n]}\hat{F}^\dagger]_C = \frac{1}{8}(l^{[n]})_{kl}^{ij} F_{\alpha\beta}^{kl*} \{i^\dagger j^\dagger \beta\alpha\}, \quad (71)$$

with

$$\hat{l}^{[n]} = \frac{1}{4}(l^{[n]})_{kl}^{ij} \{i^\dagger j^\dagger lk\}, \quad (72)$$

and $\hat{L}_0^{[n]}$ is a constant. Again, $l^{[n]}$ and F must be connected through k and l . It can be shown that

$$\hat{L}_0^{[n]} = \delta_{n0}, \quad (73)$$

and hence, for an excited state ($n > 0$), the equations that determine the unknown parameters are

$$\langle \Phi_0 | (\hat{L}^{[n]}\bar{H})_L | \Phi_i^a \rangle = \omega^{[n]}(l^{[n]})_i^a, \quad (74)$$

$$\langle \Phi_0 | (\hat{L}^{[n]}\bar{H})_L | \Phi_{ij}^{ab} \rangle = \omega^{[n]}(l^{[n]})_{ij}^{ab}, \quad (75)$$

and

$$\langle \Phi_0 | (\hat{L}^{[n]}\bar{H})_L | \Phi_{ij}^{kl} \rangle = \frac{1}{2}\omega^{[n]}(l^{[n]})_{kl}^{mn} X_{mn}^{ij}, \quad (76)$$

where $|\Phi_{ij}^{kl}\rangle$ is defined by the Hermitian conjugate of eqn (20).

For the ground state, the left-hand-side EOM-CC-R12 equations reduce to the so-called Λ equations of the CC-R12 method:³⁷

$$\langle \Phi_0 | \bar{H} + (\hat{\Lambda}\bar{H})_L | \Phi_i^a \rangle = 0, \quad (77)$$

$$\langle \Phi_0 | \bar{H} + (\hat{\Lambda}\bar{H})_L | \Phi_{ij}^{ab} \rangle = 0, \quad (78)$$

$$\langle \Phi_0 | \bar{H} + (\hat{\Lambda}\bar{H})_L | \Phi_{ij}^{kl} \rangle = 0, \quad (79)$$

where, in accordance with the convention, we use $\hat{\Lambda}$ for the deexcitation operator that is related to $\hat{L}^{[0]}$ by $\hat{L}^{[0]} = 1 + \hat{\Lambda}$, $(l^{[0]})_a^i = \lambda_a^i$, $(l^{[0]})_{ab}^{ij} = \lambda_{ab}^{ij}$, $(l^{[0]})_{kl}^{ij} = \lambda_{kl}^{ij}$ *etc.* The Λ equation is central to the calculations of analytical gradients, analytical molecular properties and certain noniterative, perturbation corrections of the effects of higher-order connected \hat{T} to lower-order CC energies.^{53–57} A preferred derivation of this equation leading to the same result is based on the CC-R12 energy functional defined, in complete analogy to the conventional CC energy functional,^{47,48} as

$$E = \langle \Phi_0 | (1 + \hat{\Lambda})\bar{H} | \Phi_0 \rangle. \quad (80)$$

Demanding that E be stationary with respect to λ_a^i , λ_{ab}^{ij} and λ_{kl}^{ij} , we arrive at the CCSD-R12 amplitude equations (17)–(19). The stationary value of E is equal to E_0 . This quasi-variational character of E makes the relevant parameters (λ_a^i , λ_{ab}^{ij} and λ_{kl}^{ij}) useful for analytical gradients and properties, whose formulae are generally simpler for variational methods. Requiring that

E be stationary with respect to t_i^a , t_{ij}^{ab} and t_{ij}^{kl} leads, on the other hand, to the amplitude equations (77)–(79).

The tensor contraction expressions defining EOM- (both right- and left-hand-side wave functions) and Λ -CC-R12 and their computational sequences are compiled as ESI† for methods through and up to the connected quadruple excitation operators (EOM- and Λ -CCSDTQ-R12). As in CC-R12, *ad hoc* common subexpression eliminations ($\tilde{r} = Fr$, $\tilde{l} = lF^*$, and $\tilde{\lambda} = \lambda F^*$) are performed after the RI insertion with the CABS. EOM- and Λ -CC-R12 introduce additional equations that determine the coefficients multiplying the r_{12} -dependent factors to what corresponds to the usual equations in EOM- and Λ -CC.

The size dependence of the operation cost of solving these additional equations [eqn (67), (76) and (79)] varies with the method (Table 8). In EOM-CC-R12 (right-hand side), it remains to be $O(n_p n_p^3 n_h^3)$ for EOM-CCSDT-R12 or higher and is, therefore, quickly surpassed by the cost of solving the usual amplitude equations in EOM-CC (right-hand side) of excitation rank k , which increases as $O(n_p^{k+2} n_h^k)$. This again suggests that eqn (67) be solved without making drastic approximations in high-rank EOM-CC-R12 (right-hand side) for achieving benchmark accuracy.

In Λ - and EOM-CC-R12 (left-hand side), in contrast, the operation cost of solving the geminal amplitude equations increases as $O(n_p^{k+1} n_h^{k+1})$. This is because $\tilde{L}^{[m]}$ in these equations is a deexcitation operator and can be contracted variously with \tilde{H} and excitation operator \hat{T} , adding significant complexity to the resulting equations, unlike \tilde{S} and $\tilde{R}^{[m]}$ that are excitation operators and cannot be contracted with \hat{T} . One of the terms with the $O(n_p^4 n_h^4)$ complexity (see Fig. 4 for its diagram) in the Λ -CCSDT-R12 geminal amplitude equation is

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = \frac{1}{4} (1 - P_{i_3 i_4}) F_{(i_1 i_2)}^{a_5 a_6} v_{a_5 a_8}^{(i_3 i_7)} t_{(i_7 i_1 i_1 i_2)}^{(a_8 a_9 a_{10})} \lambda_{(a_6 a_9 a_{10})}^{(i_4 i_1 i_1 i_2)}, \quad (81)$$

which is evaluated as

$$\delta_{(i_1 i_2)}^{(i_3 i_4)} = F_{(i_1 i_2)}^{a_5 a_6} \zeta_{a_5 a_6}^{(i_3 i_4)}, \quad (82)$$

$$\zeta_{a_5 a_6}^{(i_3 i_4)} = (1 - P_{i_3 i_4}) v_{a_5 a_8}^{(i_3 i_7)} \zeta_{i_7 a_6}^{i_4 a_8}, \quad (83)$$

$$\zeta_{i_7 a_6}^{i_4 a_8} = \frac{1}{4} t_{(i_7 i_1 i_1 i_2)}^{(a_8 a_9 a_{10})} \lambda_{(a_6 a_9 a_{10})}^{(i_4 i_1 i_1 i_2)}. \quad (84)$$

Since $\hat{\mathcal{L}}^{[m]}$ is a double deexcitation operator, the geminal amplitude equations in Λ - and EOM-CC-R12 (left-hand side) resemble the L_2 amplitude equations of Λ - and EOM-CC (left-hand side) respectively. The complexity of the latter is also $O(n_p^{k+1} n_h^{k+1})$. Because the overall peak operation cost of high-rank Λ -CC-R12 and EOM-CC-R12 (left-hand side) methods is $O(n_p^{k+2} n_h^k)$, which is greater than the $O(n_p^{k+1} n_h^{k+1})$ cost of the geminal amplitude equations, there seems no need to intro-

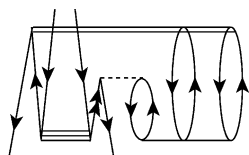


Fig. 4 The diagrammatic representation of eqn (81).

duce a further approximation to the latter. In high-rank Λ -CC-R12 and EOM-CC-R12 (left-hand side), therefore, computerized symbolic algebra such as SMITH is particularly useful because the complexity of their geminal amplitude equations grows, unlike those of CC-R12 and EOM-CC-R12 (right-hand side).

IV. Conclusions

In this study, we have derived the compact mathematical expressions for the CC-R12 methods up to CCSDTQ-R12 with the CABS and modified ansatz 2 and suggested computational sequences that reduce the peak operation and memory costs. These expressions have been automatically generated by the newly-developed computerized symbolic algebra code SMITH, which can handle Slater-determinant expectation values of any combination of excitation, deexcitation and general operators, including those that appear in the R12 ansätze. SMITH also has additional capabilities to identify and isolate the special intermediates and insert the RI approximations using the CABS, which are specific symbol manipulations in the CC-R12 derivations. We have found that certain recurring intermediates (Ft) must be precalculated, stored and reused to arrive at an efficient computational sequence, particularly in CCSD-R12. Our previous code TCE is inadequate in virtually every step of the derivation and algebraic transformation of CC-R12.

We have, furthermore, defined the ansätze for the EOM- and Λ -CC-R12 methods which are essential for the evaluation of excitation energies and analytical gradients and properties within the CC-R12 framework. We have presented the working equations and efficient computational sequences of these methods up to the models that include the connected quadruple excitation operator (EOM- and Λ -CCSDTQ-R12).

The operation costs of these methods have been examined on the basis of the suggested computational sequences. In CCSD-R12, the operation cost for solving the geminal amplitude equation [$O(n_p^3 n_h^3)$] exceeds that for solving the T amplitude equation [$O(n_p^4 n_h^4)$], supporting some approximations to simplify the former. Such approximations include SA¹³ as well as approximate CC-R12 variants.^{18,20,23,24} In the higher-order analogues, however, the operation cost for solving the geminal amplitude equations becomes increasingly less important in the overall cost; in fact, it is estimated to be negligible in the CCSDT-R12 method. The same holds for the EOM-CC-R12 (right-hand side) method. The geminal amplitude equations of the Λ - and EOM-CC-R12 (left-hand side) become increasingly involved as the excitation rank (k) is raised. The operation cost of solving the equations scales as $O(n_p^{k+1} n_h^{k+1})$ for $k \geq 3$, which is nevertheless smaller than the overall cost $O(n_p^{k+2} n_h^k)$. This suggests that the higher-order CC-R12 implementations may be based on the unabridged equations and computational sequences presented in this paper to achieve the highest accuracy with no significant penalty in the operation or memory cost.

Efforts towards automatic code generations of CC-R12 by SMITH, the code verification and validation and the performance assessment of the various models suggested here

are underway. The results will be presented in forthcoming articles.

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